Natural Organic Matter Characterization in Drinking Water

by

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LIST OF ABBREVIATIONS AND SYMBOLS USED

^{13}C-NMR	Carbon 13 Nuclear Magnetic Resonance
$Al_2(SO_4)_3$	Aluminum sulfate / alum
$Ca(OCl)_2$	Calcium hypochlorite
$CHBr_3$	Bromoform
$CHBr_2Cl$	Dibromochloromethane
Br_2CHCO_2H	Dibromoacetic acid
$BrCH_2CO_2H$	Monobromoacetic acid
$CHCl_3$	Chloroform
$CHCl_2Br$	Dichlorobromomethane
Cl_2CHCO_2H	Dichloroacetic acid
Cl_3CCO_2H	Trichloroacetic acid
Cl_2	Chlorine
$ClCH_2CO_2H$	Monochloroacetic acid
CO_2	Carbon dioxide
Daltons	Da
DBP	Disinfection by-product
DBPfp	Disinfection by-product formation potential
DOC	Dissolved organic carbon
EPA	Environmental Protection Agency
$FeSO_4$	Iron sulfate
GC–MS	Gas Chromatography – Mass Spectrometry
HAA	Haloacetic acid

HAAfp   Haloacetic acid formation potential

HIA   Hydrophilic acid

HIB   Hydrophilic base

HIN   Hydrophilic neutral

HOA   Hydrophobic acid

HOB   Hydrophobic base

HOCl   Hypochlorous acid

HON   Hydrophobic neutral

HPSEC   High pressure size exclusion chromatography

JDKWSP   J.D. Kline Water Supply Plant

MAC   Maximum acceptable concentration

MCL   Maximum contaminant level

MGD   Million gallons per day

mAU   milli-absorbance units

mV   milli-volts

MVWA   Mohawk Valley Water Authority

Mw   Molecular weight

NaOCl   Sodium hypochlorite

NOM   Natural organic matter

OCl$^-$ Hypochlorite ion

PACL   Poly aluminum chloride

pH   Potential hydrogen

SEC   (High pressure) Size exclusion chromatography

SUVA   Specific ultraviolet absorbance

THAA   Total haloacetic acid

THM	Trihalomethane
TTHM	Total trihalomethane
THMfp	Trihalomethane formation potential
TOC	Total organic carbon
UFC	Uniform formation conditions
UV_{254}	Ultraviolet

ACKNOWLEDGEMENTS

ABSTRACT

The main objective of this research was to develop an improved understanding of the types and quantities of natural organic matter (NOM) from two water sources; one supplying the JD Kline Water Supply Plant (JDKWSP) and the other supplying the Mohawk Valley Water Authority (MVWA). Both watersheds are characterized by low alkalinity, low turbidity and low organic matter content. In particular, this study looked at the chemical and physical properties of NOM. As well, the relationship between forming unwanted disinfection by-products in drinking water from NOM in the presence of chlorine and the potential to remove NOM during water treatment processes, namely coagulation, was investigated.

Ion-exchange resin fractionation was carried out on multiple 20 L samples of raw and filtered water for a period of 1 year. Fractionation allowed the separation of NOM into six unique fractions; hydrophobic and hydrophilic acids, bases and neutrals. Each fraction was analyzed for dissolved organic carbon (DOC), zeta potential, DBP formation potential (DBPfp) and molecular size distribution using high pressure size exclusion chromatography (HPSEC).

Results from the NOM characterization showed that the raw water supplying the JDKWSP was primarily comprised of hydrophobic and hydrophilic neutral compounds. The raw water supplying the MVWA, in contrast, was primarily comprised of hydrophobic acid and hydrophilic neutral compounds. The molecular weight ranges of most organic fractions were 1100 – 65 Da such that distinctions based on size could not be made. The largest compounds in the raw water were dominated by hydrophobic acid compounds at the MVWA and hydrophobic neutral compounds at the JDKWSP.

On a mass basis, the hydrophobic acid fraction contributed most to the formation of DBPs in the raw and treated water from the MVWA. Additionally, the hydrophilic neutral fraction was found to be an important THM precuror, on a mass basis, at both treatment plants. On a normalized yield basis, however, this fraction contributed little to the DBPs.

A comparison of DOC removal between the two treatment plants revealed greater removals at the MVWA. This was attributed, in large part, to the abundance of the hydrophobic acid fraction in the raw water and its preferential removal by alum. In contrast, there was little to no removal of the hydrophobic base fraction at either treatment plant. This was largely attributed to the positive surface charge exhibited by this fraction.

CHAPTER 1   INTRODUCTION

1.1.   Project Rationale

Natural organic matter (NOM), when reacted with chlorine can create a group of compounds known widely as disinfection by-products (DBPs). Mitigation of DBP can occur by reducing or removing NOM precursors through water source management, chemical/physical removal or oxidation/transformation processes (Minear and Amy, 1996).

In conventional water treatment facilities, coagulation is a critical step for achieving optimal removal of NOM and subsequent mitigation of DBPs. Additionally, coagulation performance is highly dependent on the characteristics and concentration of NOM in the source water. Specific knowledge of these characteristics can help focus removal techniques to those compounds most responsible for DBP formation.

Resin fractionation used to characterize the dissolved organic carbon (DOC) in natural waters was first described by Leenheer (1981) and later modified by Marhaba *et al.* (2003). This technique extracts and separates different classes of organic compounds based on the chemical affinities of these to specific ion-exchange resins. The classes of organics separated by this procedure are hydrophobic acid, base and neutral compounds and hydrophilic acid, base and neutral compounds. This information can more accurately determine the quantity and quality of the nonsorbable DOC during coagulation with metal salts than can current models that use the raw water SUVA and coagulant dose to predict DOC removal (Edwards, 1997). Additionally, the separation of DOC into six organic compound classes allows further analysis to determine which types of compounds are contributing most to DBP formation in a system and how well they are being removed by current treatment practices.

In addition to the chemical properties exhibited by NOM, the physical size of organic compounds also affects their removal by coagulation (Edzwald, 1994). It is well documented that lower molecular weight compounds are more difficult to remove

(Edzwald, 1994; Ratwaneera *et al,*. 1999). Thus, knowledge of the approximate molecular weight of organic compounds within different fractions can help to predict the removal of DOC by coagulation.

The uniqueness of each water source and the labor intensive nature of resin fractionation have resulted in few publications on the variations of hydrophobic and hydrophilic compounds and their response to coagulants. Several studies have pointed to humic and fulvic acids being the primary precursors to DBP formation. As a result, many site-specific studies have focused solely on quantifying these compounds. Rice and MacCarthy (1991) noted that the characteristics and concentration of NOM exhibit significant variations in molecular make up; elemental composition, functional group content, molecular weight and aromaticity between different water sources. Therefore it is important to characterize the entire natural organic matter matrix of each water source. Moreover, these studies should be repeated throughout the year as the amount and composition of natural organic matter changes seasonally (Rice and MacCarthy, 1991). Capturing the effects of changes in temperature and precipitation on the natural organic matter matrix can help predict periods where treatment plants are particularly vulnerable to increases in DOC and subsequent increases in DBPs in the treated water.

1.2.   Research Objectives

The main objective of this study was to develop an improved understanding of the type and quantities of natural organic matter in two watersheds; Lake Pockwock and the Hinkley reservoir. The ability for NOM and its specific fractions to form disinfection by-products in drinking water was studied to meet this objective. The research program was conducted in three sub-objectives described herein;

1) To characterize the natural organic matter in two watersheds over a period of time to capture seasonal variations. Characterization tools included total and dissolved organic carbon, zeta potential, resin fractionation and size exclusion

chromatography to determine the physical and chemical properties of NOM within the target watershed.

2) To determine the NOM fractions that contribute most to the formation of DBPs. The formation potential of organic fractions was evaluated seasonally and under different chlorine dosing conditions.

3) To examine the removal of organics following conventional water treatment. This was achieved by fractionating treated water and determining the DOC and DBP removal rates for each fraction compared to the raw water data.

CHAPTER 2   BACKGROUND

2.1.   Natural Organic Matter

Natural organic matter (NOM) is a heterogeneous mix of naturally occurring organic compounds. They are, in large part, the result of decaying plant and animal tissues whose type and concentration vary between water sources and seasonally within a water source (Leenheer and Croue, 2003). During warmer months, the micro-biotic community is most active in breaking down larger organic substrates, thereby producing more organic matter in the watershed (Scott *et al.,* 2001). Much of this organic matter remains trapped in the soil until rainfall events trigger runoff from shorelines. This runoff disturbs lake bottoms releasing trapped organic matter into the water column (Scott *et al.,* 2001; Hongve *et al.,* 2004). This increase in organic content in the fall has been documented by several studies (Sharp *et al.,* 2006; Malcolm, 1985). Some studies have even reported that these seasonal increases are primarily the result of increased hydrophobic organic material as compared to hydrophilic organic material (Sharp *et al.,* 2006; Malcolm, 1985).

Determining the exact nature and composition of organics present in a watershed can be quite costly (Leenheer and Croue 2003).   Analytical techniques such as gas chromatography/mass spectrophotometry (GC-MS) and carbon-13 nuclear magnetic resonance (^{13}C-NMR) can determine the specific chemical compounds and their concentrations in a sample. Depending on the nature of the research, these detailed analyses might not be required. Alternatively, characterization by fractionation is a less costly method and can provide important water quality information. Earlier research has determined the principal chemical compounds that make up each of the six organic fractions (Table 2.1). Additionally, Table 2.1 summarizes the impact of specific organic fractions on their ability to form DBPs, promote biofilm growth, their role in corrosion in distribution systems and their impact on aesthetics in drinking water.

Table 2.1 – Nature and impact of organic fractions in drinking water treatment.

Organic Fraction	Chemical Compounds	DBPfp	Biological Activity	Transport of Metals	Color	Taste & Odor
Hydrophobic Neutral (HON)	Hydrocarbons, Pesticides, Carbonyl Compounds, aldehydes, ketones, alkyl alcohols	Moderate	High	Low	None	None
Hydrophobic Acid (HOA)	Humic and Fulvic Acids, aromatic acids, high Mw carboxylic acids, phenols	High	Low	High	High	Moderate
Hydrophobic Base (HOB)	Aromatic Amines, Proteins, Amino Acids, Amino-Sugars	Moderate	High	Moderate	High	None
Hydrophilic Acid (HIA)	Sugar Acids, Fatty Acids, Hydroxyl Acids, Low Mw Carboxylic acids	N/A	N/A	N/A	Moderate	N/AN
Hydrophilic Base (HIB)	Polysaccharides, Aromatic Amines, Proteins, Amino Acids, Amino-Sugars	Moderate	High	Moderate	High	None
Hydrophilic Neutral (HIN)	Oligosaccharides, Polysaccharides, aldehydes, ketones, low Mw alkyl alcohols	N/A	N/A	N/A	N/A	N/A
References	Imai *et al.,* 2001	Croue *et al.,* 2000	Croue *et al.,* 2000	Croue *et al.,* 2000	Croue *et al.,* 2000	Croue *et al.,* 2000

The natural organic matter composition of different water sources are compared in Table 2.2. Overall, the hydrophobic acid and hydrophilic neutral fractions have been found to be the most abundant among the surface waters evaluated by other researchers (Kanokkantapong *et al*., 2005; Kanokkantapong *et al*., 2006; Korshin *et al*., 1997; Marhaba and Van, 1999; Marhaba and Van, 2000; Swietlik and Sikorska, 2005). For highly colored surface waters, the hydrophobic fraction was found to be as high as 70% of the total TOC (Korshin *et al.,* 1997).

The significance of the hydrophilic neutral organic fraction dominating over the other fractions brings into question the use of UV-254 as a surrogate for the determination of TOC (Dobbs *et al.,* 1972), coagulant dose (Edwards, 1997) and DBPfp (Li *et al.,* 2000) as this fraction exhibits low refraction to UV-254 (Labanowski and Feuillade, 2009). One study has shown the hydrophilic neutral fraction to be an important precursor to DBPs in waters with low color (Liang and Singer, 2003). Therefore a complete knowledge of the types and concentrations of natural organic matter is critical in optimizing NOM removal for the mitigation of DBPs.

Table 2.2 – Comparison of natural organic matter composition between water sources.

Reference	Swietlik and Sikorska, 2005	Marhaba and Van, 1999	Marhaba and Van, 2000	Kanokkantapong et al., 2005	Kanokkantapong et al., 2006	Korshin et al., 1997
HON	12%	21.5%	10%	0 - 12%	5.7 - 12%	0 - 25%
HOB	> 1%	5.6%	7%	0.8 - 6.8%	0.8 - 5.7%	0 - 22%
HOA	73%	11%	12%	31 - 38%	31 - 34%	19 - 68%
HIB	5%	3.4%	5%	1.4 - 5.5%	3.3 - 5.5%	1.5 - 10%
HIA	7%	44%	53%	5.9 - 18%	8 - 18%	8 - 50%
HIN	3%	19%	13%	20 - 56%	25 - 44%	1 - 35%

2.2.   Disinfection By-Products: Formation and Characterization

Disinfection by-products (DBPs) are a class of compounds formed by the reaction of natural organic matter with disinfectants used in drinking water treatment. Chlorine was the first disinfectant used in drinking water treatment and is still widely used today. Currently, chlorine is available as molecular chlorine $(Cl_2)_{(g)}$, calcium hypochlorite $[Ca(OCl)_2]_{(s)}$ and sodium hypochlorite $(NaOCl)_{(l)}$, all of which dissolve to form $Cl_{2(aq)}$ when applied to water. The aqueous chlorine disproportionates to form hypochlorous acid (HOCl) and free chlorine (Cl⁻):

$$Cl_{2(aq)} + H_2O \rightleftharpoons HOCl + H^+ + Cl^-$$
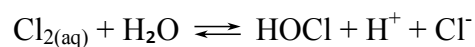
The hypochlorous acid forms an equilibrium relationship with a hypochlorite ion (OCl⁻):

$$HOCl \rightleftharpoons H^+ + OCl^-$$
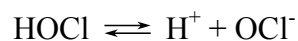
Reactions between HOCl/ OCl⁻ and NOM result in the partial oxidation of NOM and/or the incorporation of Cl⁻ into the NOM to from DBPs (Li *et al.,* 2000).   The exact mechanisms of DBP formation are not entirely understood. However, Figure 2.1 shows the proposed pathway by which chloroform is formed where R represents the organic compound (Sincero and Sincero, 2003). There has been evidence to suggest that, in the case of chloroform, this trihalomethane (THM) does not split from the parent molecule ―R" until a substantial amount of HOCl has been incorporated into the molecule (Li *et al.,* 2000).

Step 1: $R - \overset{\overset{\displaystyle O}{\|}}{C} - CH_3 \underset{OH^-}{\rightleftharpoons} R - \overset{\overset{\displaystyle O^-}{|}}{C} = CH_2 + H^+$

Step 2: $R - \overset{\overset{\displaystyle O^-}{|}}{C} = CH_2 + HOCl \longrightarrow R - \overset{\overset{\displaystyle O}{\|}}{C} - CH_2 Cl + OH^-$

Step 3: $R - \overset{\overset{\displaystyle O}{\|}}{C} - CH_2 Cl \underset{OH^-}{\rightleftharpoons} R - \overset{\overset{\displaystyle O^-}{|}}{C} = CHCl + H^+$

Step 4: $R - \overset{\overset{\displaystyle O^-}{|}}{C} = CHCl + HOCl \longrightarrow R - \overset{\overset{\displaystyle O}{\|}}{C} - CHCl_2 + OH^-$

Step 5: $R - \overset{\overset{\displaystyle O}{\|}}{C} - CHCl_2 \underset{OH^-}{\rightleftharpoons} R - \overset{\overset{\displaystyle O^-}{|}}{C} = CCl_2 + H^+$

Step 6: $R - \overset{\overset{\displaystyle O^-}{|}}{C} = CCl_2 + HOCl \longrightarrow R - \overset{\overset{\displaystyle O}{\|}}{C} - CCl_3 + OH^-$

Step 7: $R - \overset{\overset{\displaystyle O}{\|}}{C} - CCl_3 + H_2O \underset{OH^-}{\longrightarrow} R - \overset{\overset{\displaystyle O}{\|}}{C} - OH + CHCl_3$
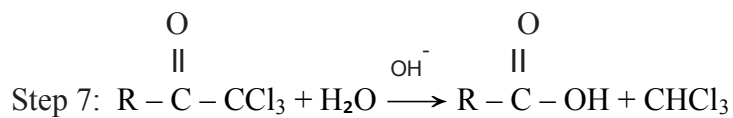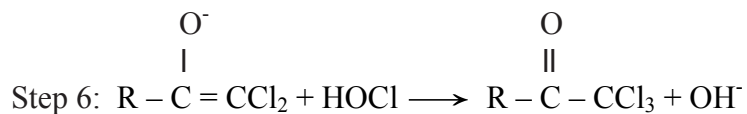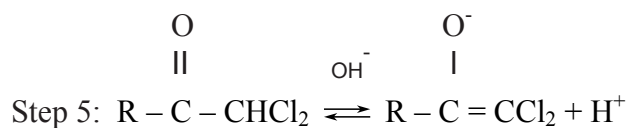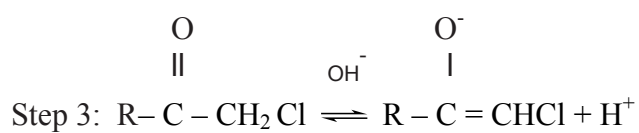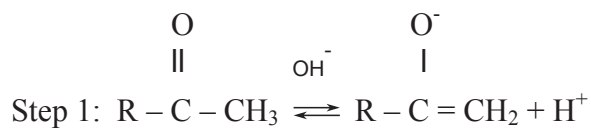
Figure 2.1 – Proposed scheme for chloroform formation as presented by Sincero and Sincero (2003).

Among the DBPs discovered thus far are trihalomethanes (THMs), haloacetic acids (HAAs), haloacetonitriles, haloketones and halopicrin (Nikolaou *et al.,* 1999). THMs and HAAs are the most abundant DBPs, by mass, in surface waters. They were first identified in drinking water by Dutch Scientist Johannes Rook in 1974 and have since been extensively studied for their potential health risks to humans. Early studies exposing mice to THMs and HAAs have reported high incidences of cancer (Health Canada, 2006). They have since been shown to be carcinogenic, mutagens and toxicants in laboratory studies (Health Canada, 2006). Additionally, epidemiology studies have found correlations between DBP exposure and adverse birth outcomes (Bove *et al.,* 1995; Chisholm *et al.,* 2008; Nieuwenhuijsen *et al.,* 2008) as well as bladder, colon, and rectal cancers (King and Marrett, 1996; Hildesheim *et al.,* 1998). Bromodichloromethane, a THM, has been shown to be particularly toxic at concentrations approaching 20 µg/L (King *et al.,* 2000; Dodds *et al.,* 2004).

Health Canada (2006) has stipulated maximum acceptable concentrations (MAC) for disinfection by-products at 0.1 mg/L for total THMs (TTHMs) and 0.08 mg/L for total HAA$_5$ (THAA$_5$). Nova Scotia has adopted these recommendations and incorporated them into provincial legislation under the *Water and Wastewater Facilities and Public Drinking Water Supplies Regulation* (1994). These levels reflect an annual average of a minimum of four samples taken at a point in the distribution system where the highest levels occur. Regulation of THMs in drinking water, in Canada, began in 2006 whereas monitoring of HAAs only began in 2008. In the United States, the Environmental Protection Agency (EPA) has imposed more strict regulations for DBPs (2006). The *Safe Drinking Water Act* stipulates maximum contaminant levels (MCL) of 0.08 mg/L for THMs and 0.06 mg/L for HAAs (USEPA, 2006). Table 2.2 shows the specific THM and HAA compounds and their chemical abbreviations currently regulated by both Canada and the United States.

Table 2.3 – Regulated THM and HAA and their abbreviated chemical structures.

Trihalomethanes		Haloacetic Acids	
Chloroform	$CHCl_3$	Monochloroacetic acid	CH2ClCO2H
Dichlorobromomethane	$CHCl_2Br$	Dichloroacetic acid	$CHCl_2CO_2H$
Dibromochloromethane	$CHBr_2Cl$	Trichloroacetic acid	CCl_3CO_2H
Bromoform	$CHBr_3$	Monobromoacetic acid	CH_2BrCO_2H
		Dibromoacetic acid	Br_2CHCO_2H

Several factors can affect the formation of THMs and HAAs in drinking water; the type and concentration of NOM and the chlorination pH, temperature, concentration, point of addition and contact time (Liang and Singer, 2003; Nikolaou *et al.,* 1999). Increasing the concentration of NOM increases the disinfection by-product formation potential (DBPfp). The specific chemical structure of NOM that promotes the formation of DBPs, however, is less understood. Aromatic organics and humic acids have been studied extensively and have been shown to be principal DBP precursors (Liang and Singer, 2003; Nikolaou *et al.,* 1999; Edwards, 1997). This was generalized by Croue *et al.* (2000) stating that the more hydrophobic and acidic in nature the NOM, the greater the DBPfp. Recent research however is showing the importance of the hydrophilic organic fraction as being an important precursor to DBPfp particularly in waters with low humic content (Liang and Singer, 2003).   In particular, the hydrophilic organic fraction was found to be more reactive to bromide (Br⁻) than any other fraction (Liang and Singer, 2003).

The pH of chlorination can also affect the types and quantities of DBPs in a system as this influences the stability and concentration of HOCl ions. At a pH greater than 8 (Nikolaou *et al*., 1999), hydroxyl ions dominate and remove protons from organic material, allowing chlorine to be incorporated as shown in Figure 2.1. Increases in pH result in an increase in THMfp (trihalomethane formation potential) and a decrease in HAAfp (haloacetic acid formation potential) whereas decreasing the pH has the reverse effect (Nikolaou *et al.,* 1999; Liang and Singer, 2003). Increasing water temperature, at

the point of chlorination, results in faster reactions between NOM and chlorine. Thus, increasing the chlorine demand of the water subsequently increases the DBPfp (Nikolaou et al., 1999; Liang and Singer, 2003). The point of addition of chlorine will also impact the formation of DBPs. Chlorine added after NOM removal in a treatment plant will result in lower DBP levels in the treated water than plants that pre-chlorinate prior to NOM removal. Finally the contact time between chlorine and NOM will ultimately affect the DBPfp. Increasing contact time increases both THMs and HAAs formation potentials (Nikolaou et al., 1999; Liang and Singer, 2003).

2.3.   Mitigating Disinfection By-Products

The best way to mitigate DBPs in drinking water is to remove as much NOM as possible prior to the addition of chlorine. While several different treatment options have been developed to remove NOM, the focus of this research will center on removal by coagulation.

In surface water, natural organic matter remains stable and suspended in the water column as a result of their relatively small size and the mutual repulsion forces exerted by similarly charged compounds. This inability to settle, or settle very slowly by gravity alone requires the addition of a chemical to destabilize the colloids thereby facilitating precipitation of the NOM. Traditionally, metal salts such as aluminum sulphate or alum [$Al_2(SO_4)_3$], ferric sulfate ($FeSO_4$) and polyaluminum chloride or PACl [$Al_2(OH)_nCl_{6-n}$] have been used to neutralize the electrical double layer surrounding organic and inorganic particles, allowing them to bind to the coagulant itself or to other colloids (Sincero and Sincero, 2003). The addition of the coagulant is applied through a rapid mix stage to evenly disperse the chemical throughout the water. This procedure is followed by a slow mixing stage orflocculation process, allowing particles to agglomerate to form flocs. Both the chemical and physical properties of NOM have been shown to affect this process. The total and dissolved organic content, the amphiphilicity, the zeta potential, the total surface charge and the molecular weight of organic colloids have been identified

as important factors affecting/explaining variances in the coagulant treatment efficacy of NOM.

In 1997, a model was developed by Edwards to predict DOC removal during enhanced coagulation. He noted that there were two types of DOC; sorbable and non-sorbable to a coagulant. Furthermore these fractions could be predicted from the raw water specific ultraviolet absorbance (SUVA) calculated according to Equation 2.1:

$$SUVA_{raw} = 100 \times \{[UV_{254}\ (cm^{-1})] / DOC\ (mg/L)\} \qquad Eq\ 2.1$$

The non-sorbable fraction has been attributed to the hydrophilic organic fraction of NOM (White *et al*., 1997; Edwards, 1997; Sharp *et al.,* 2005; Fearing *et al,*. 2004). This fraction is typically comprised of lower molecular weight colloids that exhibit significantly lower charge density than the hydrophobic organic fraction (Collins *et al.,* 1986; Edzwald, 1993; Ratnaweera *et al.,* 1999). This low charge density is thought to interact less with the cationic metal hydroxides formed during coagulation resulting in little or no destabilization of these types of colloids (Edzwald, 1993). Others studies have corroborated these findings by showing that the coagulation of NOM favors larger hydrophobic organics which exhibit a high charge density (Gu *et al.,* 1995; Huang and Shiu, 1996; Sharp *et al.,* 2005). Several studies have also proposed that optimization of coagulation processes should be based on the colloidal and total surface charge of the water rather than SUVA alone (Fearing *et al.,* 2004; Sharp *et al.,* 2005).
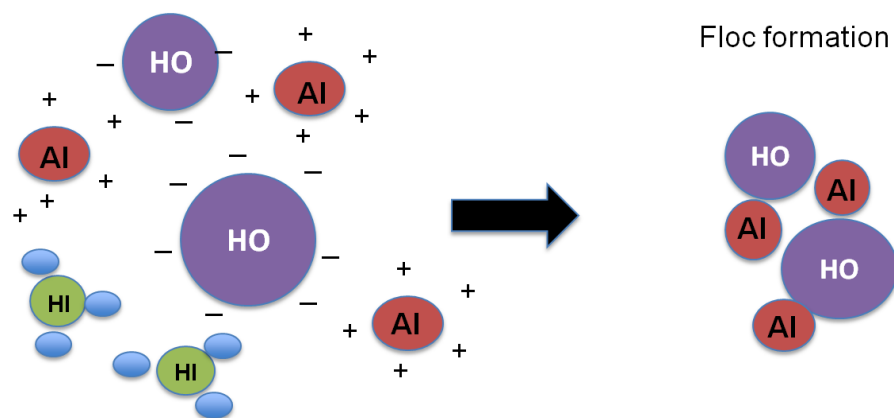
Figure 2.2 – Interaction between alum and hydrophobic/hydrophilic organic compounds.

CHAPTER 3   MATERIAL & METHODS

3.1.   Source Water Characteristics

The source water analyzed in this study were supplied by two water treatment plants with similar raw water qualities; the J.D. Kline Water Supply Plant (JDKWSP) and the Mohawk Valley Water Authority (MVWA) treatment plant. An overview of the raw and treated water qualities as well as a description of the treatment process, of each facility, are presented in this section.

3.1.1. Overview of the JDKWSP

The JDKWSP, located in Upper Hammonds Plains, Nova Scotia, produces on average 20 MGD and serves several communities throughout the Halifax Regional Municipality. The plant draws its water from Pockwock Lake, a fairly pristine and protected watershed, with little anthropogenic influence. The plant's treatment process includes pre-screening, oxidation, pre-chlorination, coagulation, hydraulic flocculation, filtration through dual media (sand/anthracite) filters and chlorination. Coagulation of the raw water occurs at a pH of 5.5 to6 and an average alum dose of 8 mg/L.

The raw and treated water quality report from the JDKWSP is presented in Table 3.1. The raw water is characterized as low turbidity, low alkalinity, low color and low DOC. From the 2009 water quality data published by Halifax Water, the treated water is in compliance with current MAC for DBPs, regulated in Canada, however there is a desire to reduce levels further to meet U.S. regulations for HAAs.

Table 3.1 – Water quality reported by the JD Kline Water Supply Plant in 2009.

Parameters	Raw Water	Treated Water
Alkalinity (as mg/L $CaCO_3$)	< 1.0	18
Color (True Color Units)	16	3
Conductivity (μmho/cm)	39	87
Hardness (as mg/L $CaCO_3$)	5.3	13.3
pH	5.6	7.3
Turbidity (NTU)	0.3	< 0.1
Total Organic Carbon (mg/L)	2.9	1.4
THM (μg/L)	< 1	73
HAA5 (μg/L)	< 5	70

3.1.2. Overview of the MVWA Treatment Plant

The MVWA treatment plant is located in Utica, New York. It produces on average 19 MGD and serves 130,000 customers. The plant draws its water from the Hinckley Lake which is fed by the West Canada Creek.   The plant's treatment process includes coagulation, flocculation using in-line static mixers, absorption clarifiers, dual media filtration and chlorination.   Alum is used during coagulation at variable dosages, depending on the raw water quality.   The pH of coagulation during sampling periods, presented in this study, varied between 5.9 to 6.3 and the dose of alum varied between 17.5 to 30.0 mg/L.

The raw and treated water quality report from the MVWA is presented in Table 3.2.   The raw water is characterized as low turbidity, low alkalinity, moderate color and low to moderate DOC. Based on the 2009 water quality data published by Mohawk Valley, the treated water was in compliance with current MCLs for THMs in the United States however they exceeded MCLs for HAAs (Table 3.2)

Table 3.2 – Water Quality reported by Mohawk Valley Water Authority in 2009.

Parameters	Raw Water	Treated Water
Alkalinity (as mg/L CaCO$_3$)	13	45
Color (True Color Units)	44	11
Conductivity (μmho/cm)	38.1	140
Hardness (as mg/L CaCO$_3$)	14	19
pH	6.6	9.1
Turbidity (NTU)	1.4	0.6
Total Organic Carbon (mg/L)	5.54	1.79
THM (μg/L)	N/A	25
HAA (μg/L)	N/A	63

Table 3.3 – Comparison of treatment strategies adopted by the JDKWSP and the MVWA.

	JDKWSP	MWVA
Treatment Plant	Direct filtration	Conventional filtration
Pre-Chlorination	Yes	No
Coagulant	Alum	Alum
Coagulating pH	5.5 to 6.0	5.9 to 6.3
Alum Dose	8 mg/L	17.5 to 30 mg/L
Mixing	Hydraulic	Mechanical
Clarifying step	No	Yes
Filtration	Dual media (sand/anthracite)	Dual media (sand/anthracite)
Disinfectant	Chlorine	Chlorine

3.2.   Raw and Filtered Water Characterization

Twenty liters of raw and plant filtered water were collected from both treatment plants over the course of a year. The raw water sampled for this study was obtained from the

pump house of both treatment plants prior to the addition of any chemicals. The treated water was obtained from both treatment plants following filtration but prior to the addition of chlorine, fluorides and polyphosphates.

The raw and filtered water were samples were analyzed for UV_{254}, organic carbon temperature, pH and conductivity before and after filtration through a Micron-PES, polysulfone, 0.45 μm filter cartridge.

3.2.1. Fractionation

Using the fractionation procedure developed by Leenheer (1981) and later modified by Marhaba *et al.* (2003), the dissolved organic matter from the raw and filtered water was separated into six organic fractions; hydrophobic acid (HON), base (HOB) and neutral (HON) and hydrophilic acid (HIA), base (HIB) and neutral (HIN). Diaion WA10 resins and Supelite™ DAX-8 resins were procured from SUPELCO (Park Bellefonte, PA). AG-MP 50 resin was procured from Bio-Rad Laboratories (Mississauga, ON). New DAX-8 resins were passed through a 500 μm sieve to remove large resins. The resin was then stored in 0.1M sodium hydroxide (NaOH) for 24 hours before sequential 24 hour cleanings with hexane and acetone using a soxhlet extractor (Leenheer 1981). The clean resins were then packed into 2.5 x 120 cm Kontes Chromaflex chromatography columns. The resins were further cleaned and prepared by passing methanol, 0.1M NaOH, 0.1M hydrochloric acid (HCl) and MiliQ through each column (Leenheer, 1981). Resin quantities in each column were determined using the resin absorption quantities calculated by Leenheer (1981). Additional resin cleaning and preparation instructions for Diaion WA10 and AG-MP 50 resins can be found in Leenheer (1981).

Before passing the sample through each column, the conductivity and absorbance (UV-254) of the MiliQ effluent were determined to ensure a conductivity of < 10 μs/cm and an absorbance < 0.001 cm^{-1}. Additionally, DOC samples were collected to determine the DOC of the resin bleed prior to passing the water sample through. Figure 3.1 describes the separation procedure used in this study. The left-hand axis describes the pH to which

the sample was adjusted prior to passing through the columns. The right hand axis describes the eluent used to desorb the desired organic material from the resins. The horizontal axis describes the order in which water was passed through each of the five columns. A photograph of the actual column setup is shown in Figure 3.2.
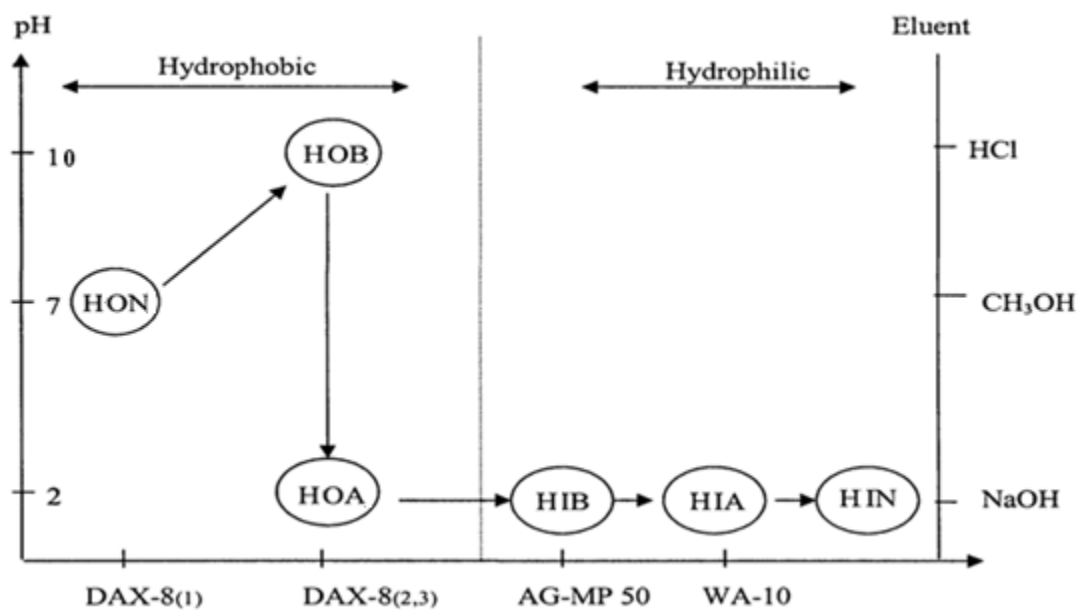
Figure 3.1 – Schematic for the resin fraction procedure adapted from Marhaba *et al.* (2003).
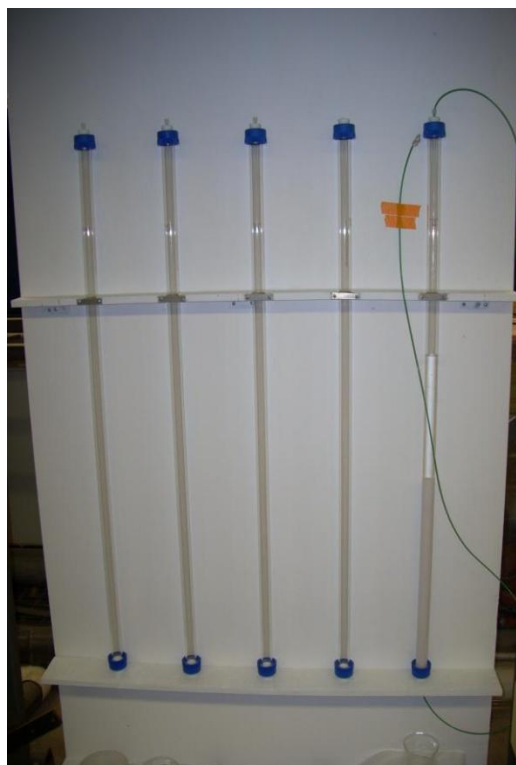
Figure 3.2 – Experimental setup of the fractionation procedure.

3.2.2. Size Exclusion Chromatography

The molecular weight distribution of organic fractions was determined using high pressure size exclusion chromatography (HPSEC or SEC). Samples were brought to a pH of 3 to 7 and passed through a 0.45 µm filter membrane (GE Water & Process Technologies). Samples were evaluated using a TSK G3000SW column (7.5 mm X 300 mm) with a TSKgel SW guard column (7.5 mm X 70 mm). The media in the TSK column consisted of silica with a pore size of 10 µm. These columns were connected to the Perkin Elmer Series 200 Autosampler and the Perkin UV/Vis detector which was set at UV 254 nm. Samples of 20 µL were injected and passed through the columns at a flow rate of 0.7 mL/min. A sample run time of 30 min was established, whereby all of the compounds in the sample had passed through the column. The molecular weight (Mw) of organics was determined by size calibration using four sodium polystyrene sulfonate standards (Scientific Polymer Products Inc) with different molecular weights;

14900, 7540, 5180 and 1530 Daltons. A coefficient of determination $R^2 > 0.90$ was consistently achieved.

3.3. Analytical Techniques

3.3.1. Total and Dissolved Organic Carbon

Total and dissolved organic carbon (TOC, DOC) samples were analyzed using a Shimadzu TOC-Vcph Total Organic Carbon Analyzer whereby organics are oxidized into carbon dioxide (CO_2) and measured as TOC.

The TOC samples were prepared by placing the sample in 50 mL head-space free vials and acidified below a pH of 2 with phosphoric acid. DOC samples were first filtered through a 0.45 μm filter paper (Cole-Parmer® Nylon Membranes) before acidifying and placing it in the vial.

3.3.2. Conductivity, Temperature and pH

Conductivity, temperature and pH were measured using an Accumet Excel XL50. Both the conductivity and pH probes were calibrated daily using standard buffer solutions from Fisher Scientific. The temperature probe was also calibrated daily using a mercury thermometer.

3.3.3. Disinfection By-Product Formation Potential

Trihalomethane and haloacetic acid formation potentials (THMfp and HAAfp) were analyzed for each of the six organic fractions extracted at each sampling event. THM and HAA samples were prepared following Standard Methods (5710) with minor

modifications (APHA, 1995). Samples were buffered to a pH of 8 with borate and stored for 24 hours after dosing with chlorine. Chlorine dosing was examined under two conditions; uniform formation conditions (UFC) and plant dosing conditions. All samples collected from the JDKWSP were dosed at 1 mg/L of free chlorine to simulate plant chlorine dosing conditions. UFC was also conducted at the JDKWSP in the month of August 2010. Chlorine dosing under UFC varied between samples such that the residual chlorine, after a 24 hour incubation period, was 1 ± 0.4 mg/L. Samples from MVWA were analyzed for UFC and plant chlorine dosing conditions. Plant dosing was 2.5 mg/L of chlorine for the months of May, June and August and 3.5 mg/L for the month of October.

THM and HAA samples were further prepared for gas chromatography analysis using liquid-liquid extraction with pentane and *tert*-butyl methyl ether (MTBE) respectively. Gas chromatography using a Varian CP-3800 GC and a Varian CP-8400 auto-sampler, coupled with an electron capture detector (GC-ECD) were used for the detection of THMs and HAAs according to the US EPA Methods 551.1 and 552.2 (Hodegson and Cohen, 1990).

GC measurements were analyzed using a Hewlett Packard 5890 Series II – Plus GC equipped with a DB-5 column and a DB-1701 column. Four THMs were measured; chloroform, dichlorobromomethane, dibromochloromethane and bromoform. Nine HAAs were measured; chloroacetic acid, bromodichloroacetic acid, dichloroacetic acid, trichloroacetic acid, bromochloroacetic acid, dibromoacetic acid, bromodichloroacetic acid, chlorodibromoacetic acid and tribromoacetic acid.

3.3.4. Zeta Potential Analysis

The surface charge of raw water organic fractions was measured using a Malvern ZetaSizer 2000 outfitted with an MPT-2 Autotitrator (Malvern, UK). The zeta potential of samples was measured every 0.2 pH units between a range of 2 to 10. Samples were pH adjusted to either acidic (pH of 2) or basic (pH of 10) conditions prior to analysis.

CHAPTER 4   RESULTS

4.1.   Seasonal Variation in the Composition of NOM

The composition of NOM was determined by resin fractionation of raw and treated water samples from both the MVWA and the JDKWSP. The hydrophobic acid, base and neutral fractions are abbreviated as HOA, HOB, and HON respectively. The hydrophilic acid, base and neutral organic fractions are abbreviated as HIA, HIB and HIN respectively. The DOC of fractions, sampled from the JDKWSP from June 2009 – January 2010, was calculated from the difference in DOC before and after passing the sample through an analytical column;

$$DOC_{HON} = DOC_{RAW} - DOC_{Column\ 1\ effluent} \qquad\qquad Eq\ 4.1$$

$$DOC_{HOB} = DOC_{Column\ 1\ effluent} - DOC_{Column\ 2\ effluent} \qquad\qquad Eq\ 4.2$$

For the remaining samples, the DOC of fractions was calculated from the concentrated DOC extracted from the column and known sample volumes;

$$C_{conc\ fraction} V_{conc\ fraction} = C_{fraction} V_{column\ influent} \qquad\qquad Eq\ 4.3$$

This change in procedure was necessary as some of the cleaning solutions used on the resins (methanol, hexane and acetone) were bleeding into the samples and creating high DOC readings in the column effluents.

4.1.1.   Seasonal NOM Variation at the JDKWSP

The raw source water feeding the JDKWSP had an average TOC of 2.5 mg/L, nearly all of which was in the dissolved form. The TOC and DOC remained fairly stable through the 12-month study except in the fall where an increase DOC of approximately 1 mg/L was observed (Figure 4.1). Despite changes in TOC and DOC, the raw water appeared to be largely hydrophobic and hydrophilic neutral in nature with some exceptions, notably

the months of July and August 2010. During these months, the hydrophobic acid and hydrophilic neutral fractions were most abundant. The relative abundance of all other fractions was highly variable between sampling events.
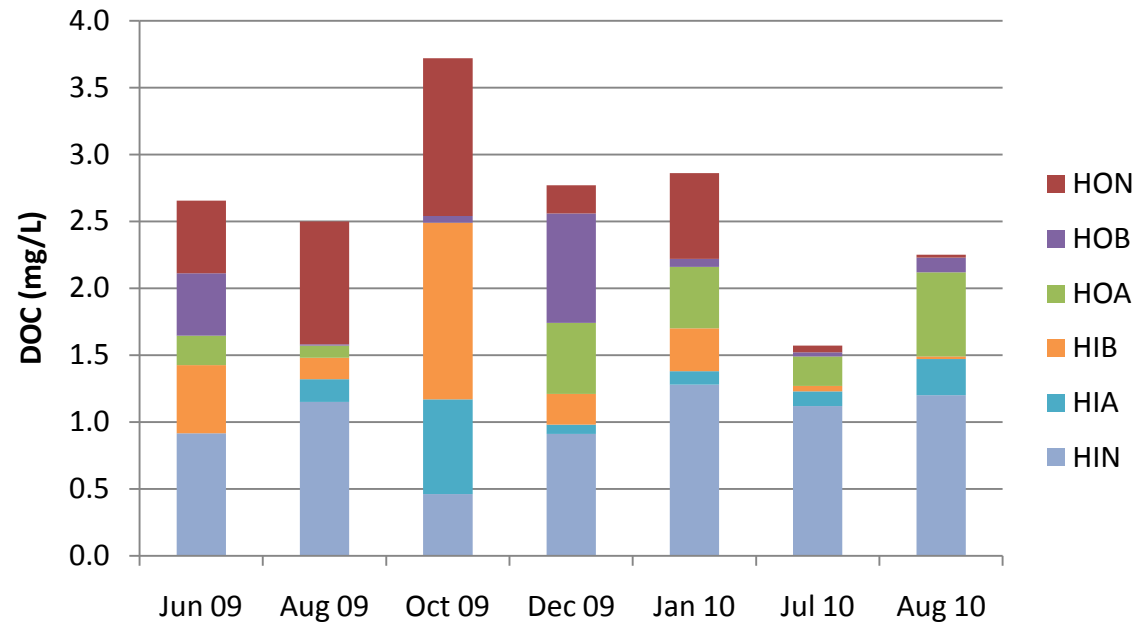
Figure 4.1– Seasonal variation of raw water DOC fractions sampled from the JDKWSP.

4.1.2. NOM Removal at the JDKWSP

Organic fractions were first grouped into two categories, hydrophobic and hydrophilic, to determine the removal of DOC within each of these fractions. Figure 4.2 shows the raw and treated water DOC composition of these fractions. Removal of DOC was largely attributed to the removal of hydrophilic organic compounds; 0.3 mg/L in July and 0.5 mg/L in August, 2010. The removal of hydrophobic organics was more variable. In July, there was an increase of 0.3 mg/L in the DOC of hydrophobic organics in the treated water. In contrast, ~0.3 mg/L of DOC from the hydrophobic fraction was removed from samples analyzed in August.

The six organic fractions were then evaluated for their contribution to the DOC in the treated water (Figure 4.3). Removal of DOC from the raw water was 0.6 mg/L and 0.5 mg/L in the months of July and August 2010 respectively. These DOC removals were calculated based on the DOC concentrations of the raw and treated water. Results show that the treated water was largely hydrophilic neutral for both sampling events (35% in July and 40% in August). In July, the hydrophobic base fraction accounted for approximately27% of the total DOC and in August, the hydrophobic acid fraction accounted for approximately 32 %. The remaining DOC, 38% in July and 28% in August, was a mix of all other fractions.

Comparing the organic composition of the raw water to the treated water, ~50 % of the hydrophilic neutral fraction was removed during treatment (Figures 4.1 & 4.3). There was 73% removal of the hydrophobic acid fraction during July 2010. This removal, however, was reduced to 25% in August, 2010. The portion of hydrophilic acid and base and the hydrophobic neutral fractions remained virtually unchanged after treatment, suggesting these fractions were not as easily removed during treatment.
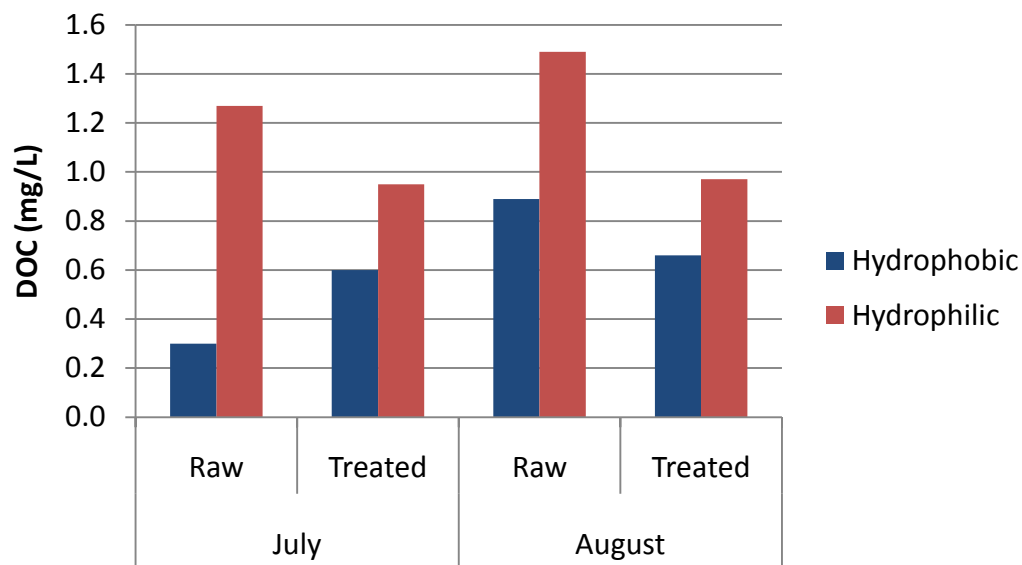
Figure 4.2 – Organic composition of raw and treated water sampled from the JDKWSP.
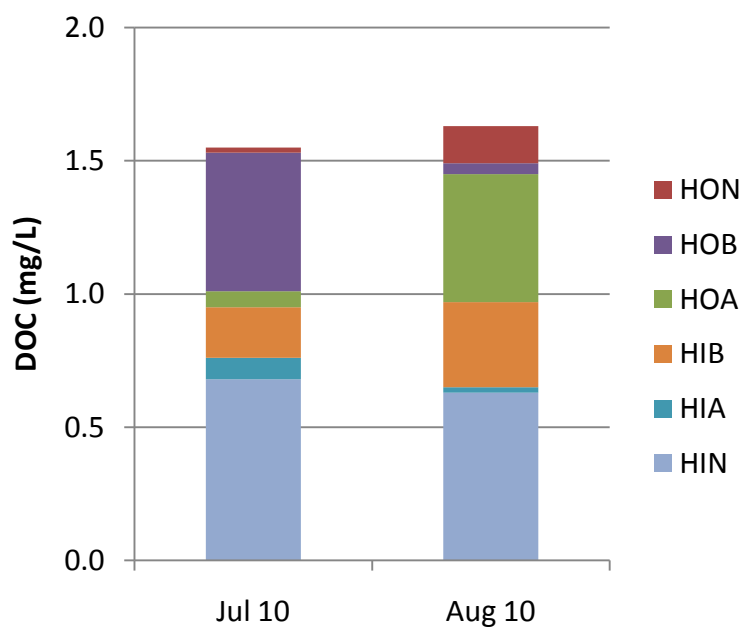
Figure 4.3 – Organic composition of treated water sampled from the JDKWSP.

4.1.3.   Seasonal NOM Variation at the MVWA

The raw source water feeding the MVWA had a much more variable TOC and DOC over sampling events (Figure 4.4). The average TOC and DOC concentrations were 5.5 mg/L and 4.9 mg/L respectively. The sample taken in the month of October saw the greatest increase in DOC, ~ 2.5 mg/L above the average. The organic composition was largely comprised of hydrophobic acids (35% on average) and hydrophilic neutral organic fractions (33% on average). Increases in DOC in August and October were primarily due to increases in the hydrophobic acid fraction.

4.1.4.   NOM Removal at the MVWA

Figure 4.5 shows the hydrophobic and hydrophilic composition of the raw and treated from the MVWA.   Removal of DOC was largely attributed to the removal of hydrophobic organic compounds; 50% removal in August and 75% removal in May and October. However, an increase in the treated water hydrophobic fraction was found in June. Similarly, increases in the hydrophilic DOC composition in the treated water were found in May, June and August. In October, 45% of the DOC in the hydrophilic fraction was removed.

The six organic fractions were then evaluated for their contribution to the DOC in the treated water (Figure 4.6). The treated water sampled from the MVWA was comprised, largely, of hydrophilic fractions. In particular the hydrophilic neutral fraction appeared to be the dominant fraction. Removal of the hydrophobic fraction was attributed to removals of the hydrophobic acid fraction.   The increases in DOC in the treated water were attributed, primarily, to increases in DOC within the hydrophilic neutral fraction.
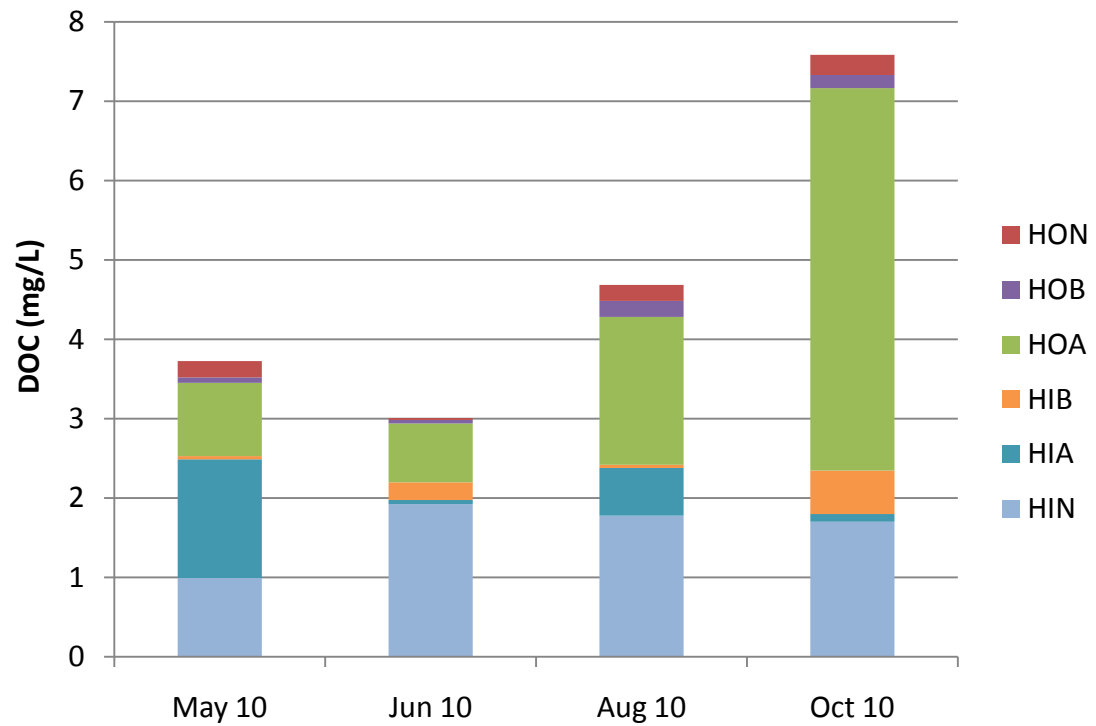
Figure 4.4 – Seasonal variation and composition of raw water DOC fractions sampled from the MVWA.
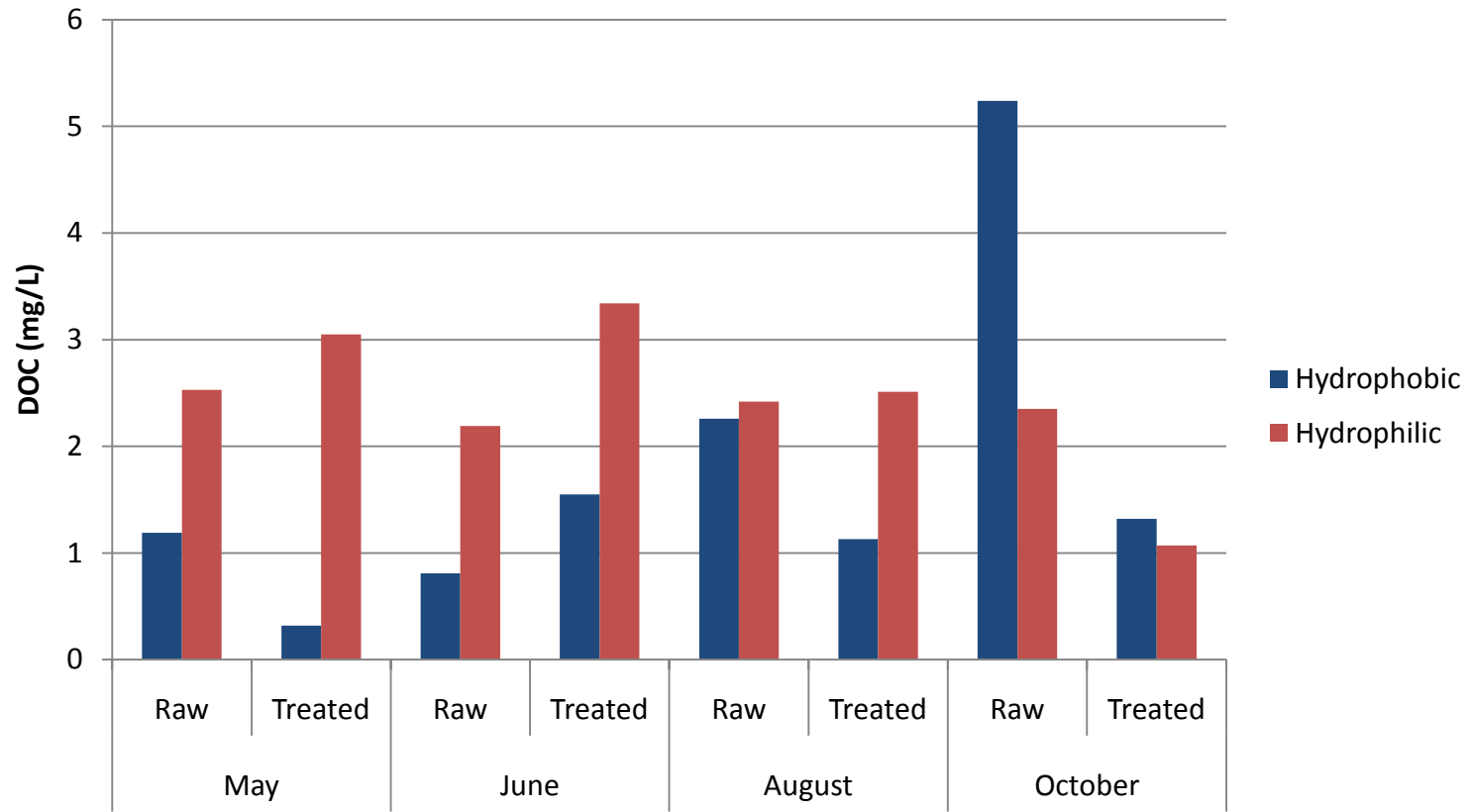
Figure 4.5 – Organic composition of raw and treated water organic fractions sampled from the MVWA.
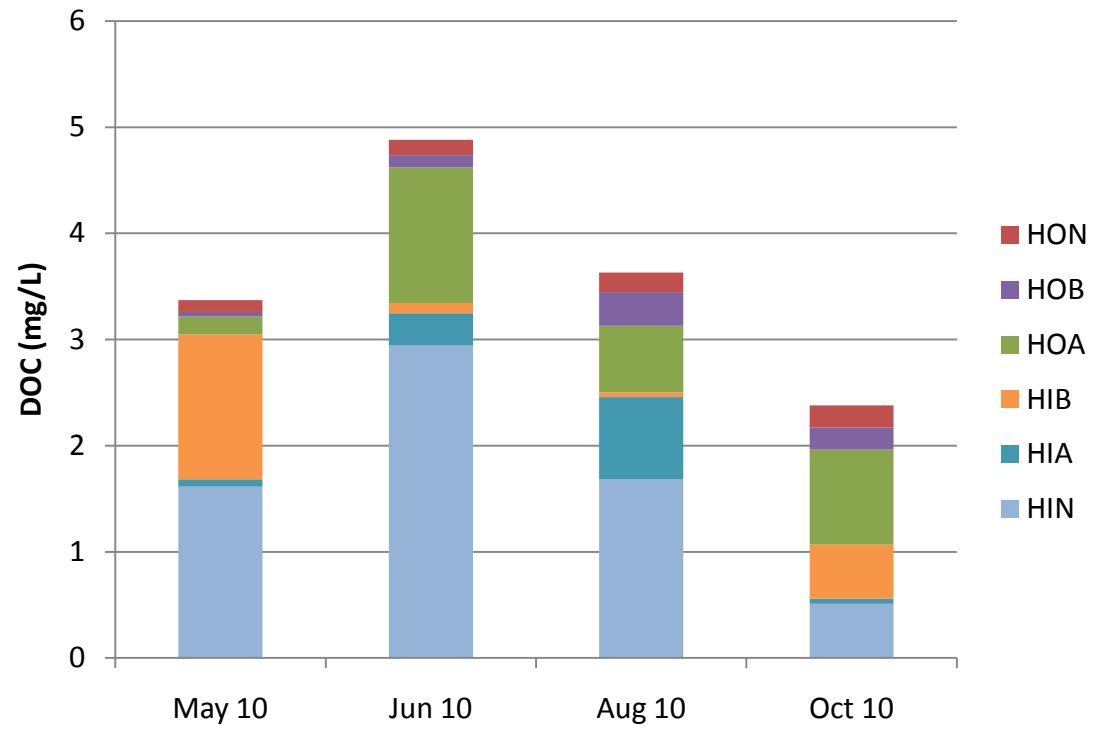
Figure 4.6 – Organic composition of treated water organic fractions sampled from the MVWA.

4.2.   Molecular Size Variation of NOM

The molecular size distribution of each organic fraction was determined using size exclusion chromatography. Peaks were identified in the raw water elution curve and labeled on each of the chromatograms. The average molecular weight associated with each of these peaks was calculated and presented in Tables 4.1 & 4.2.   In the chromatograms, the x-axis shows the elution time of the sample through the analytical gel column and the y-axis measures its refractoriness at UV_{254}, measured as milli-absorbance units (mAU). Using standards of known molecular weights, a regression was determined and used to relate the elution time of samples to molecular weights, measured in Daltons (Da). The relative removal of refractive organics matter can be determined by integrating the area under the elution curves for the raw and filtered water samples. It should be noted that the area under the elution curves for the organic fractions cannot be integrated to determine approximate removal rates as these samples have been concentrated during the fractionation process. Thus the area under the elution curve for the specific fraction may be much larger than that for the raw water as the fraction is more concentrated for a specific molecular size.

4.2.1.   NOM Size Variation at the JDKWSP

The average molecular weights associated with peaks 1 through 8 for the samples collected from the JDKWSP are presented in Table 4.1. The trends described herein were consistent for all sampling events however only SEC chromatograms for samples collected in August are presented. Peaks 6 and 7 reflect compounds present in the baseline elution curve and are not necessarily compounds found in the water samples from the JDKWSP.

Figure 4.7 shows the elution curves for the raw and treated water samples collected in the month of August 2010. Peak 1, comprised of compounds in the range of ~53,000 Da and peak 2, comprised of compounds in the range of ~ 1000 Da, were present in the raw water. These peaks, however, were not expressed in the treated water elution curve

suggesting they were removed during treatment of the raw water. The relative removal of refractive organics from the raw water was found to be 51% in July and 53% in August.

Table 4.1 – Average molecular weight of corresponding peaks represented in the JDKWSP chromatograms.

Peak	Molecular Weight (Daltons)
1	53 000 ± 6 600
2	1000 ± 190
3	740 ± 65
4	500 ± 40
5	310 ± 50
6	220 ± 25
7	140 ± 20
8	105 ± 15
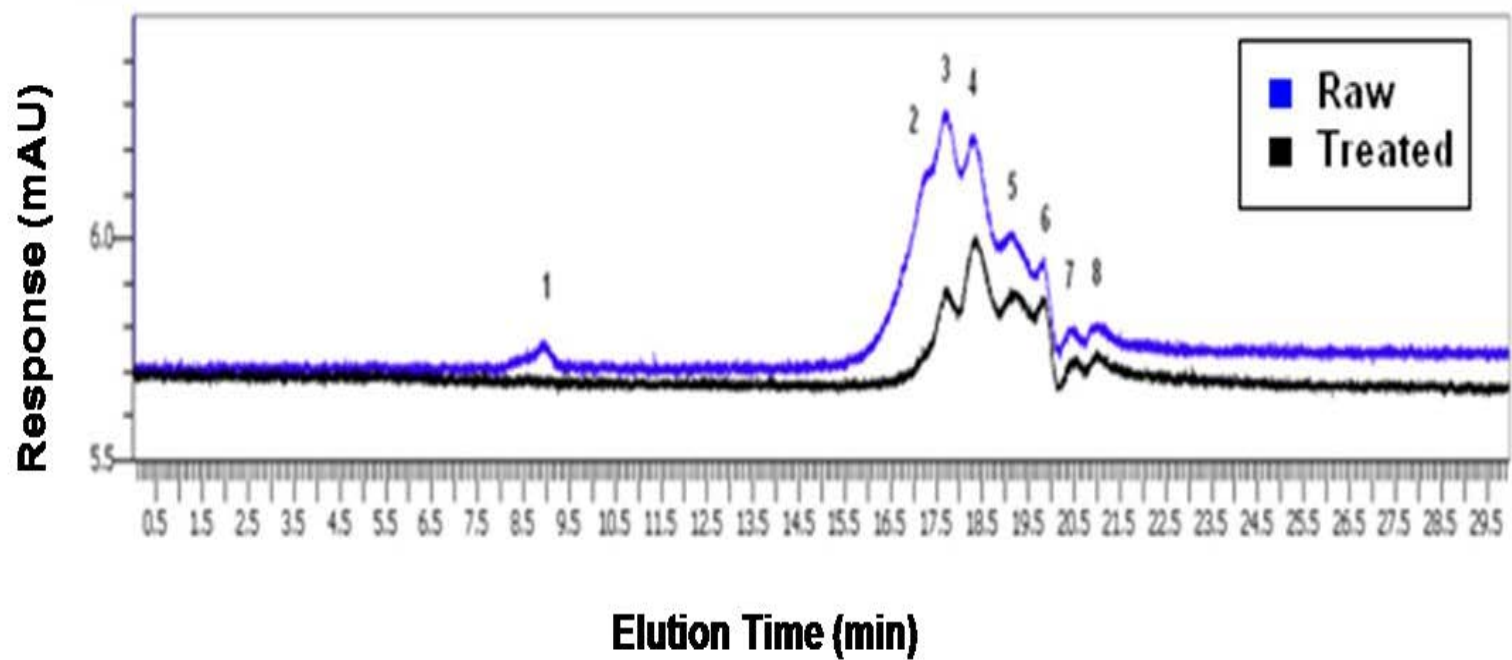
Figure 4.7 – SEC chromatogram of raw and treated water sampled from the JDKWSP in August 2010.

The elution curves of raw water and the hydrophobic fractions, extracted from the raw water, are presented Figure 4.8. Peaks were difficult to identify for the hydrophobic base and neutral fractions as these tend to be less refractive, however, analysis of each peak separately allows one to distinguish the presence of compounds in each of these fractions. Molecular weights and corresponding peaks for all fractions sampled can be found in Appendix B. Peak 1, expressed in the raw water elution curve was comprised of hydrophobic neutral organic compounds as this peak was only expressed by that fraction's elution curve. Peak 2, representing compounds of molecular weights in the range of 1000 Da was expressed by the hydrophobic acid fraction. Peaks 3 to 8, representing compounds of molecular weights in the ranges of 105-740 Da was expressed by all of the hydrophobic fractions.

Figure 4.9 shows the elution curves of raw water and the hydrophilic fractions extracted from the raw water. These fractions were comprised of smaller compounds. The hydrophilic acid and base fractions were expressed by peaks 3 to 8, representing compounds in the molecular weight range of 105-740 Da. The hydrophilic neutral fraction however was only expressed by peaks 4 to 8, representing compounds in the molecular weight range of 105 to 500 Da.

Comparatively, Figures 4.10 and 4.11 show the elution curves for the treated water and hydrophobic and hydrophilic fractions respectively. Results from the elution curves indicate that the only removal, by size, was of peak 1.
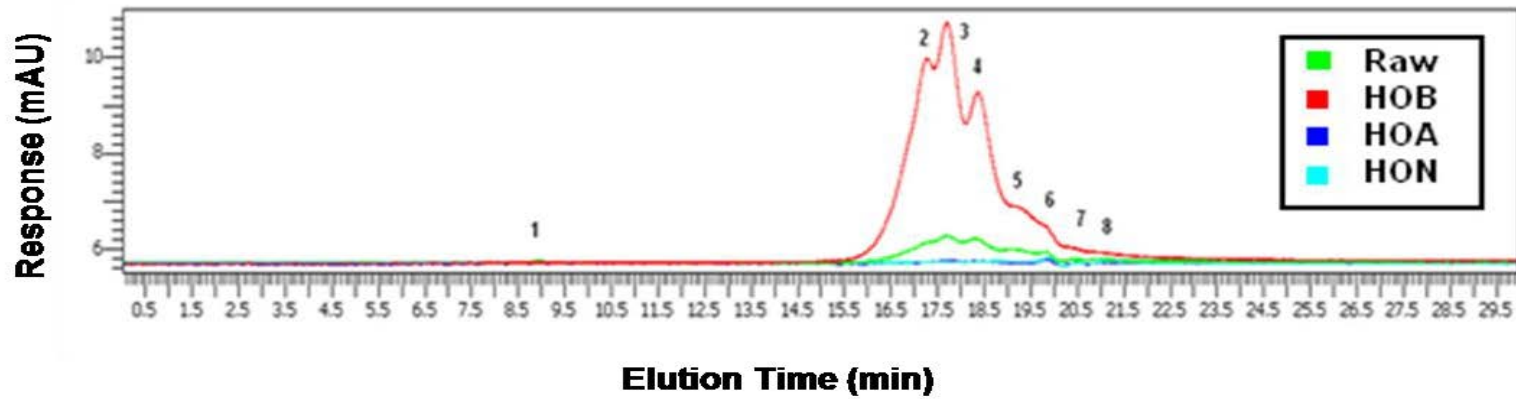
Figure 4.8 – SEC chromatogram of raw water and hydrophobic fractions sampled from the JDKWSP in August 2010.
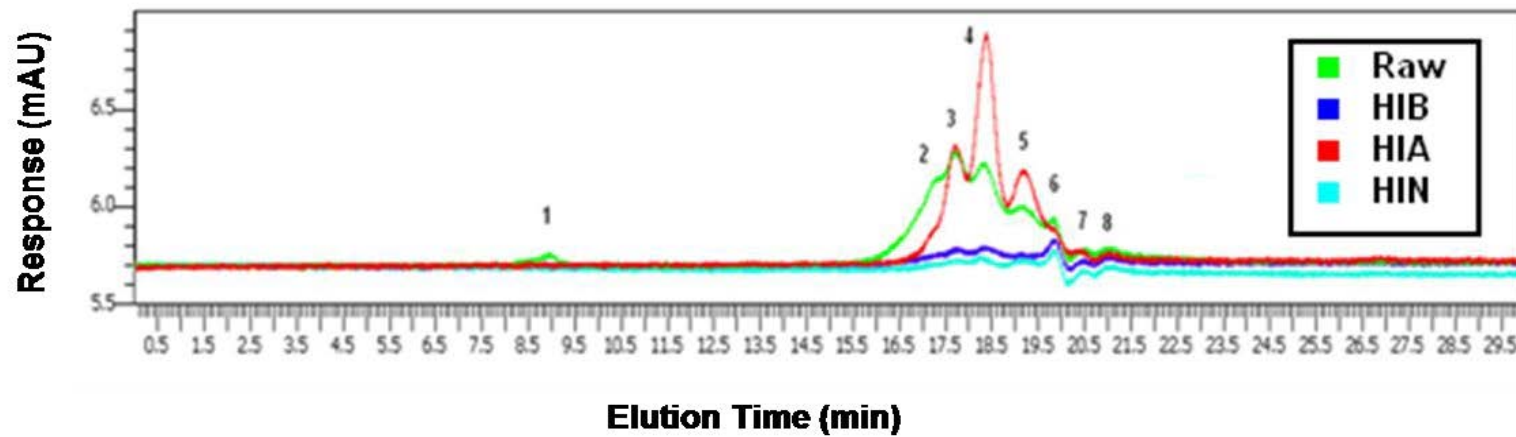
Figure 4.9 – SEC chromatogram of raw water and hydrophilic fractions sampled from the JDKWSP in August 2010.
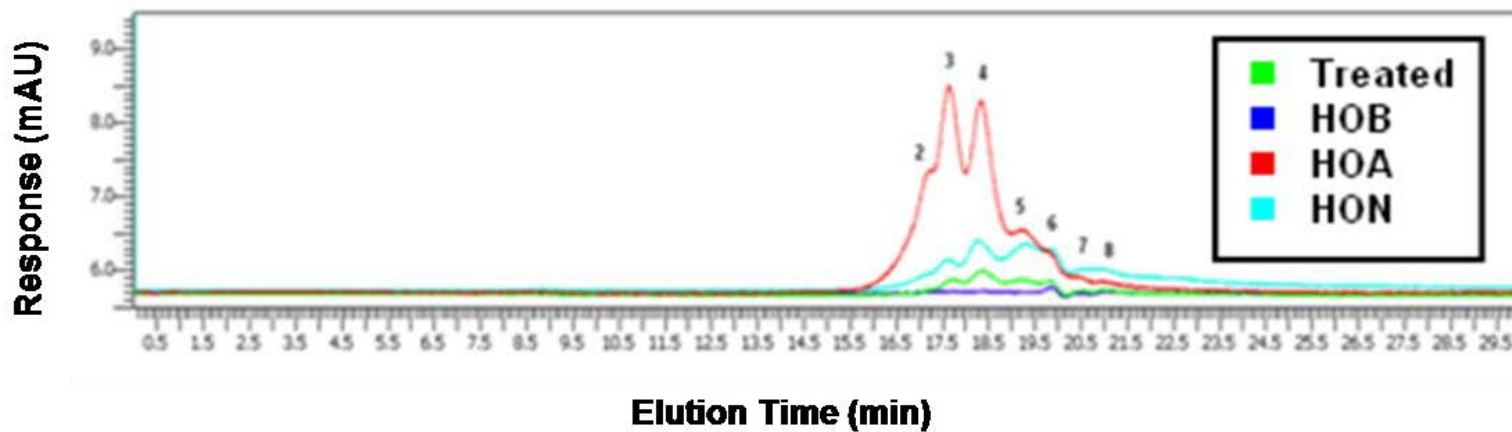
Figure 4.10 – SEC chromatogram of filtered water and hydrophobic fractions sampled from the JDKWSP in August 2010.
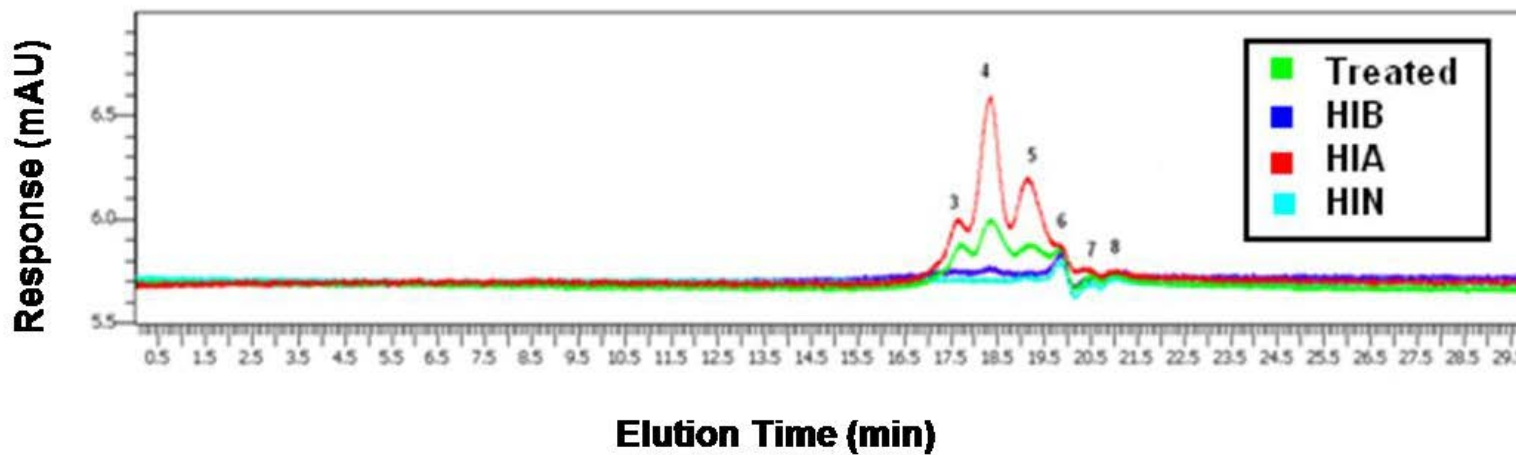
Figure 4.11 – SEC chromatogram of filtered water and hydrophilic fractions sampled from the JDKWSP in August 2010.

4.2.2. NOM Size Variation at the MVWA

The average molecular weights associated with peaks 1 through 9 for the samples collected from the MVWA are presented in Table 4.2. The trends described herein were consistent for all sampling events; however, only SEC chromatograms for samples collected in August are presented. Peaks 7 and 8 reflect compounds present in the baseline elution curve and are not necessarily compounds found in the water samples from the MVWA. Figure 4.12 shows the elution curves for the raw and treated water sampled in the month of August 2010. The elution curve for raw water expressed an early peak (peak 1) corresponding to an average molecular weight of 60,000 Da. This peak was not expressed in the elution curve of the treated water indicating removal of this size fraction. Peak 2 was also removed during treatment and a large part of the refractive organics making up peak 3. Figure 4.12 also shows that a significant proportion of refractive organics (68.9%) were removed during the treatment process. This removal rate was fairly consistent for each of the sampling events.

Table 4.2 – Average molecular weight of corresponding peaks represented in the MVWA chromatograms from samples taken in August 2010.

Peak	Molecular Weight (Daltons)
1	60000 ± 1600
2	4000 ± 250
3	1100 ± 140
4	810 ± 70
5	570 ± 60
6	350 ± 50
7	240 ± 25
8	170 ± 20
9	120 ± 20
10	65 ± 25
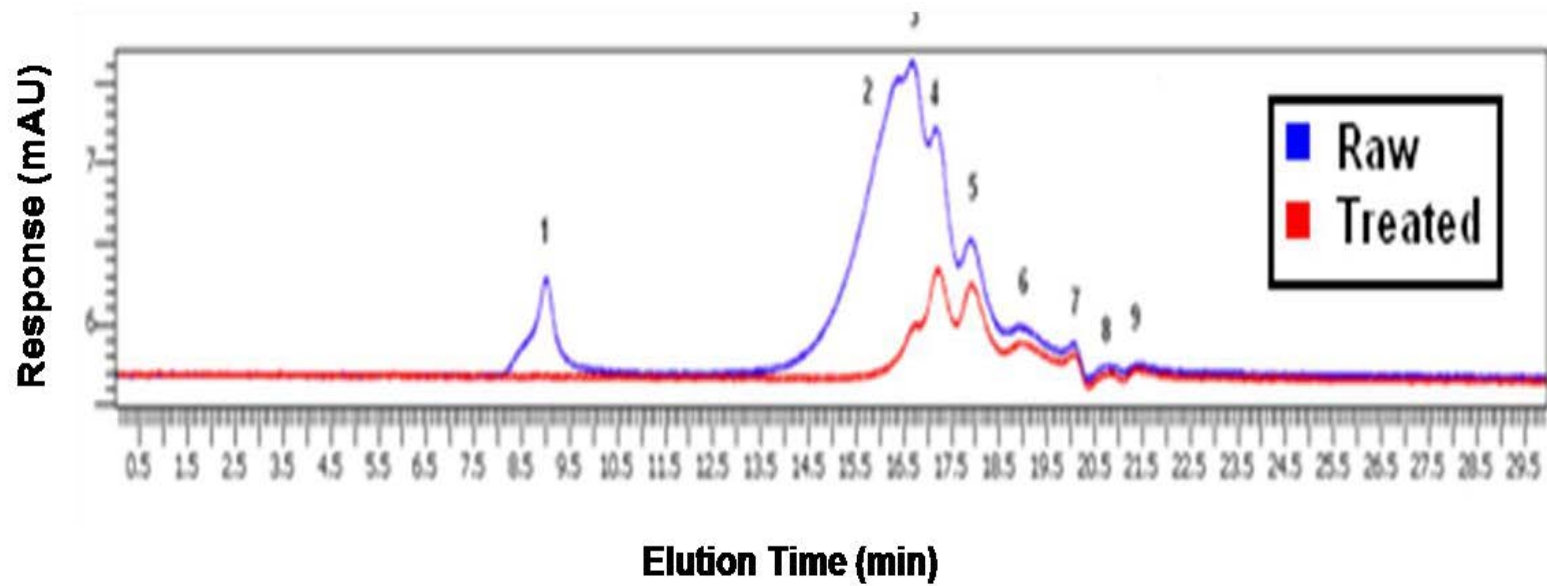
Figure 4.12 – SEC chromatogram of raw and filtered water sampled from the MVWA in August 2010.

The elution curves for the raw water and the hydrophobic organic fractions are presented in Figure 4.13. Peak 1 was expressed by the raw water and the hydrophobic acid elution curves indicating that the large organic compounds in raw water were comprised of hydrophobic acid organics. Additionally, this peak 1 was not expressed in the elution curve for the filtered water sample indicating the removal of this size fraction during treatment. The hydrophobic base and neutral fractions were expressed by peaks 2 to 9, indicating these organics were comprised of compounds with a large molecular weight range.

Similarly, Figure 4.14 shows the elution curves for the raw water and the hydrophilic organic fractions. These fractions were comprised of smaller compounds; the hydrophilic acid and neutral fractions were expressed by peaks 4-9, representing compounds in the molecular weight ranges of 65-810 Da. Comparatively, the hydrophilic base fraction was expressed by peaks 3-9, representing compounds in the molecular weight ranges of 65-1100 Da.

The elution curves for the treated water and the hydrophobic and hydrophilic organic fractions are presented in Figures 4.15 and 4.16. The hydrophobic acid fraction was only expressed by peaks 3-9 in the treated water elution curve, indicating removal of the larger compounds represented by peaks 1 and 2. The hydrophobic base and neutral fractions were expressed by peaks 3-9, indicating removal of organics expressed by peak 2 in the raw water elution curve.

A new peak was created in the treated water elution curve (peak 10) suggesting that smaller compounds are being formed following treatment of the raw water. This peak cannot be identified on the chromatogram due to the resolution. Analysis of individual fractions however revealed these peaks to be hydrophilic in nature. These fractions were comprised of smaller molecules (peaks 3-10) with lower average molecular weights of less than ~1109 Da (Figure 4.16).
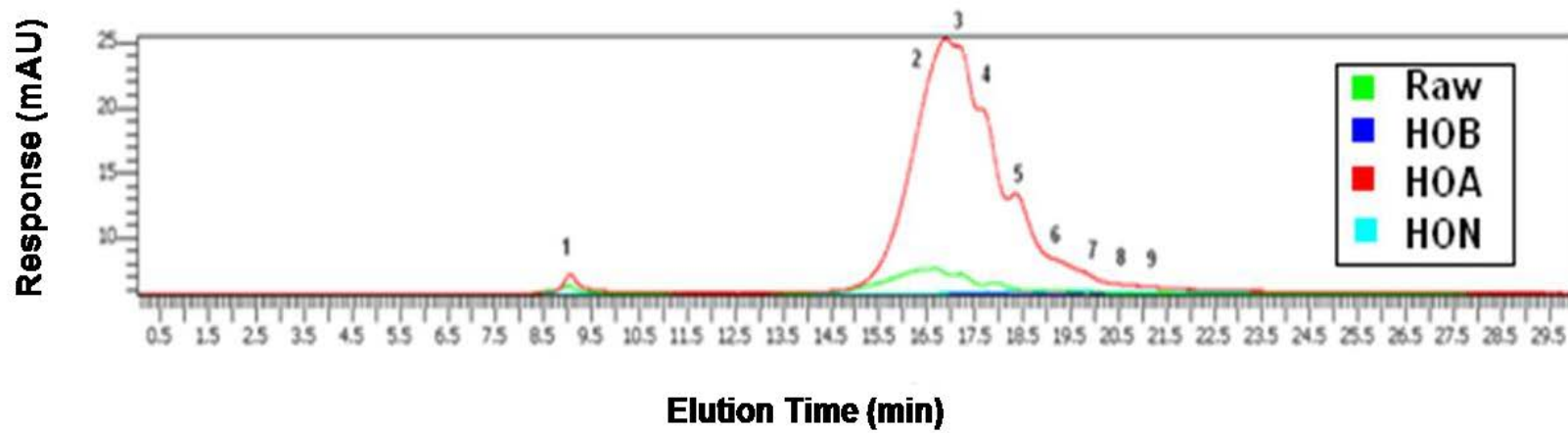
Figure 4.13 – SEC chromatogram of raw water and hydrophobic fractions sampled from the MVWA in August 2010.
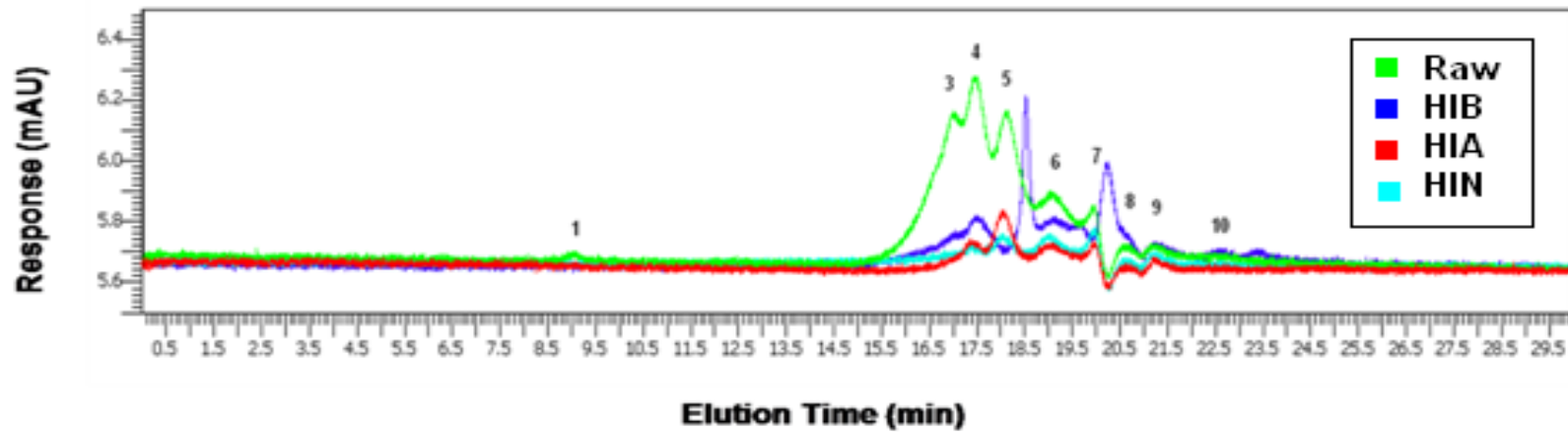
Figure 4.14 – SEC chromatogram of raw water and hydrophilic fractions sampled from the MVWA in August 2010.
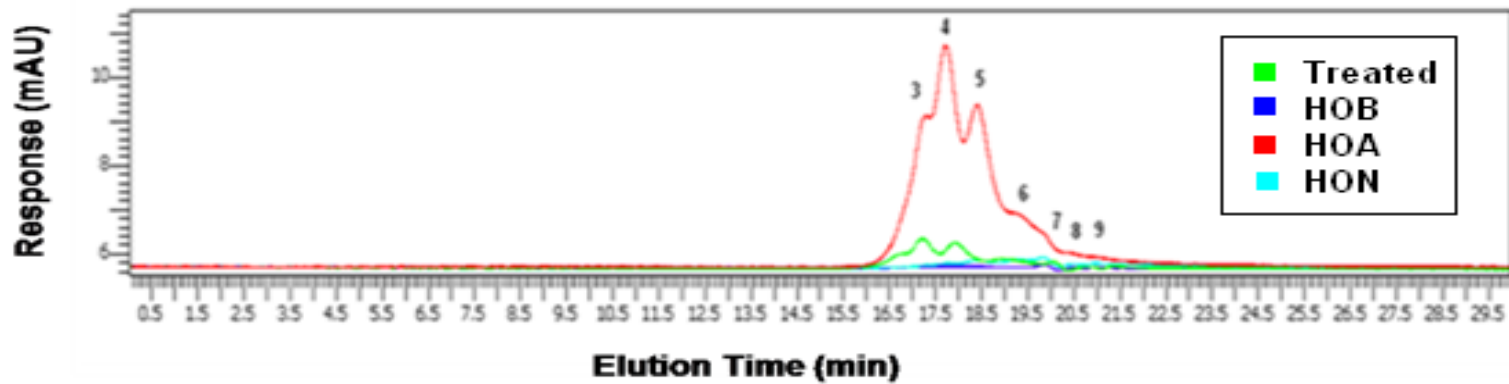
Figure 4.15 – SEC chromatogram of filtered water and hydrophobic fractions sampled from the MVWA in August 2010.
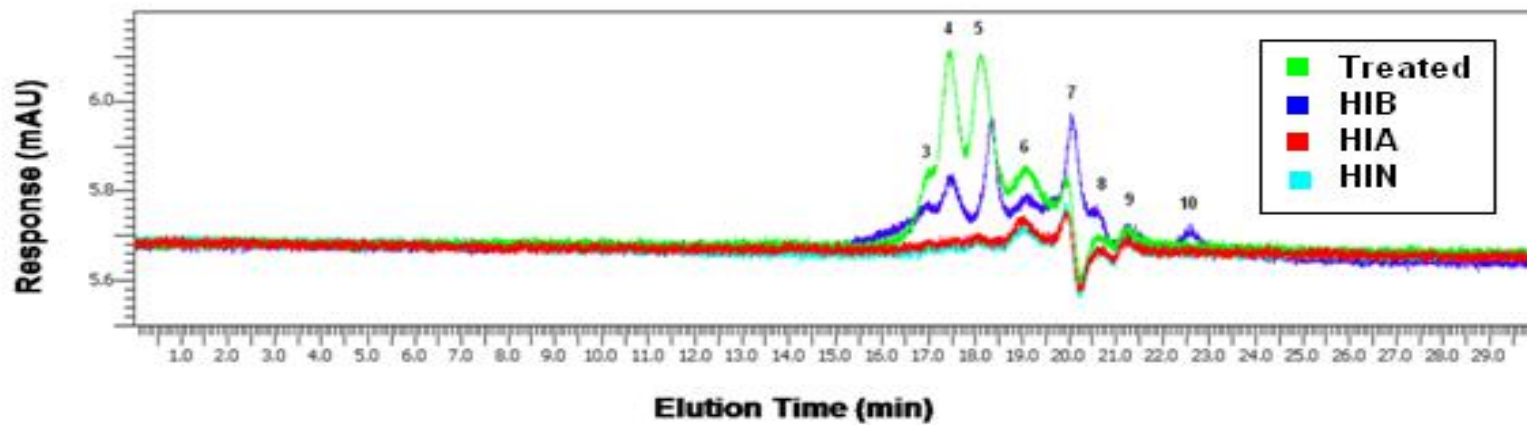
Figure 4.16 – SEC chromatogram of filtered water hydrophilic fractions sampled from the MVWA in August 2010.

4.3.   Zeta Potential Analysis on NOM

Zeta potential analysis was conducted on all of the raw water samples and associated organic fractions for samples collected in August 2010 from both the JDKWSP and the MVWA.   In this section, preliminary results are presented. Each point on the graphs represent the zeta potential measured at a particular pH and the lines between points represent the weighted mean zeta potential.

4.3.1.   Charge Analysis of NOM at the JDKWSP

Figures 4.17 and 4.18 show the isoelectric titration curves of raw water hydrophobic and hydrophilic fractions, respectively, from the JDKWSP. The pH of the raw water was 5.6 and its zeta potential was -15 mV, thus exhibitng an overall negative surface charge. At low pH, the surface charge approached neutral (-2 mV). As the pH was increased to 10, the surface charge decreased to -30 mV. This general trend was also seen for the hydrophobic neutral and acid fractions as well as the hydrophilic fractions (Figures 4.17 & 4.18). The hydrophobic base fraction, however, had a positive surface charge at pH 2 to 3 and 5.4 to 10 (Figure 4.17). A maximum negative charge of -5 mV was observed at a pH between 4 to 5.
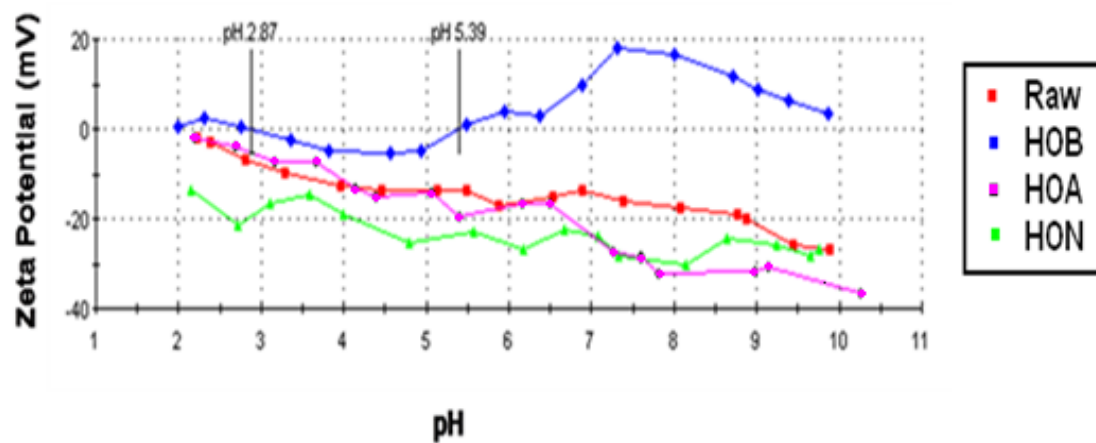
Figure 4.17 – Isoelectric titration curve of raw water and hydrophobic fractions sampled from the JDKWSP in August 2010.
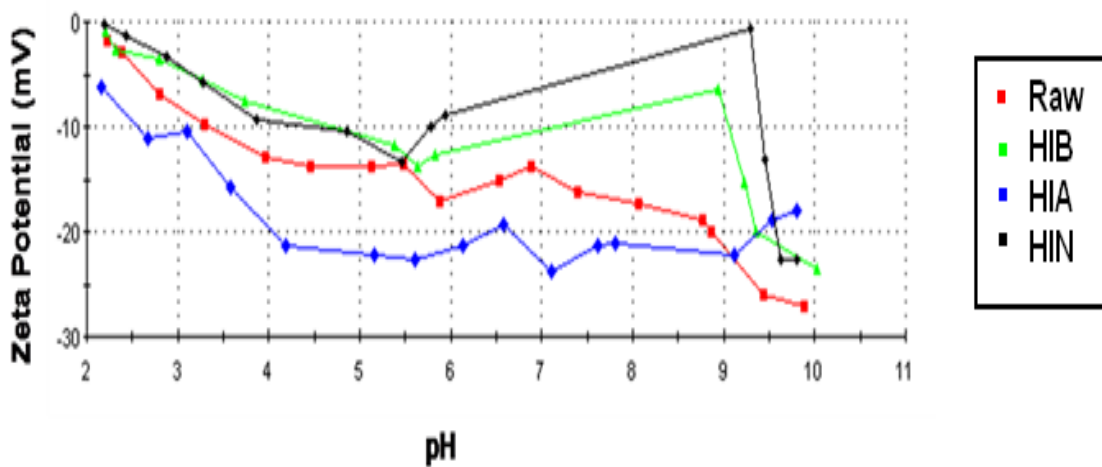
Figure 4.18 – Isoelectric titration curve of raw water and hydrophilic fractions sampled from the JDKWSP in August 2010.

4.3.2. Charge Analysis of NOM at the MVWA

Figures 4.19 and 4.20 show the isoelectric titration curves of raw hydrophobic and hydrophilic fractions, respectively, from the MVWA. The pH of the raw water was 5.83, and the zeta potential was measured to be -20 mV. At low pH, the surface charge approached neutrality. As the pH increased, the surface charge decreased to a maximum of -30 mV at a pH of 10. This general trend was observed for all fractions except for the hydrophobic base and the hydrophilic neutral fractions.

The surface charge of the hydrophobic base fraction was positive at pH 2 to 3 and 4.8 to 9.9. A maximum negative surface charge was observed at a pH of 3.8. The hydrophilic neutral fraction also had a positive surface charge between pH of 7.1 to 8.7.
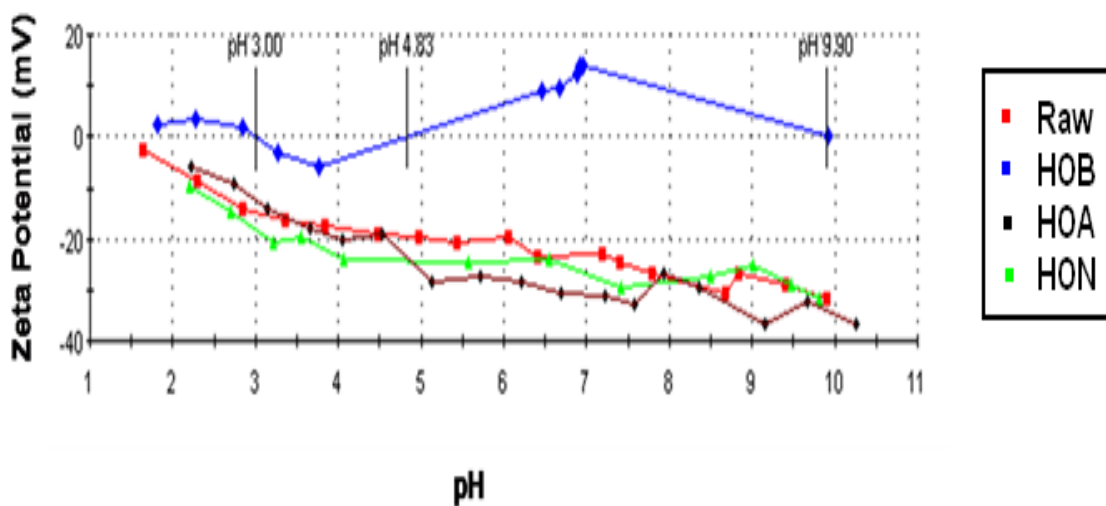
Figure 4.19 – Isoelectric titration curve of raw water and hydrophobic fractions sampled from the MVWA in August 2010.
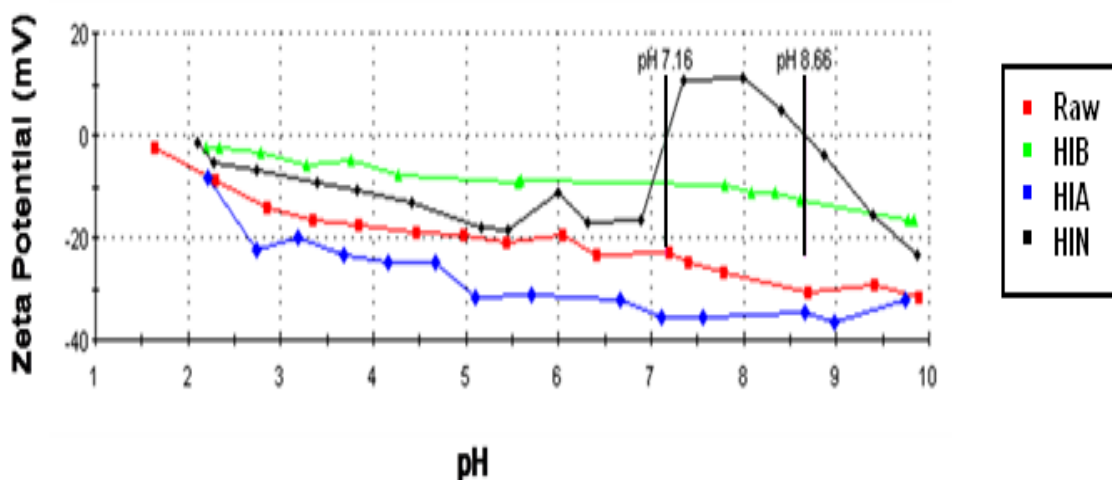
Figure 4.20 – Isoelectric titration curve of raw water and hydrophilic fractions sampled from the MVWA in August 2010.

4.4.   Disinfection By-Product Formation Potential of NOM

4.4.1. THMfp of NOM at the JDKWSP

The total trihalomethane formation potential (THMfp) for raw and filtered water from the JDKWSP dosed under plant operating conditions is presented in Figure 4.21.   The THMfp of raw water was found to be between 25 – 44 µg/L over the sampling period with little variance.   Chloroform was found to be the largest contributor to the total THMfp for each sampling event with concentrations between 7 – 36 µg/L. In contrast, no bromoform was found in the raw water samples and dibromochloromethane was only reported in the months of July and December 2009 and August 2010 in amounts less than 10 µg/L. The total THMfp of the treated water was 73 µg/L and 91 µg/L for the months of July and August respectively. Chloroform was once again found to be the greatest contributor to the total THMfp with concentrations greater than 50 µg/L. No bromoform was reported in the treated water for either sampling event.
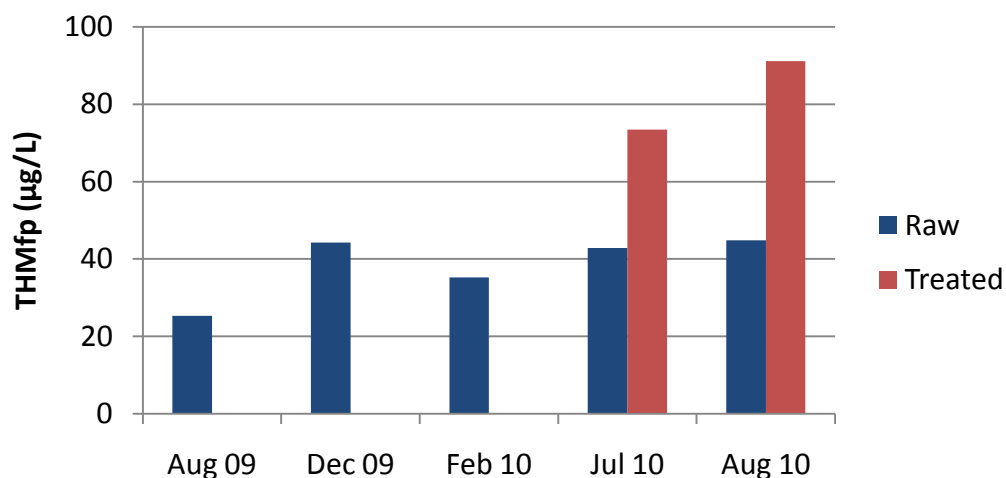
Figure 4.21 – Total trihalomethane formation potential of raw and filtered water samples from the JDKWSP (plant dosing conditions).

4.4.2. THMfp of Organic Fractions at the JDKWSP

Figure 4.22 shows the total THMfp of raw and treated water hydrophobic and hydrophilic organic fractions collected from the JDKWSP. The results are presented on a normalized yield basis; that is the total THMfp (µg/L) for every 1 mg/L of DOC. This representation is necessary as the reconstituted organic fractions are more concentrated than those typically found in the raw and treated water samples. It also allows the direct comparison of formation potentials from one fraction to another to determine which compounds have the greatest DBPfp. Additionally, the total THMfp are shown for samples dosed under plant operating conditions.

There were small decreases in the THMfp of the hydrophobic fraction in the treated water compared to the raw water; 8 µg/L in July and 15 µg/L in August. In contrast, there was a greater THMfp in the treated water hydrophilic fraction than in the raw water. Overall, it was found that the hydrophillic fraction contributed most to the THMfp in the treated water.
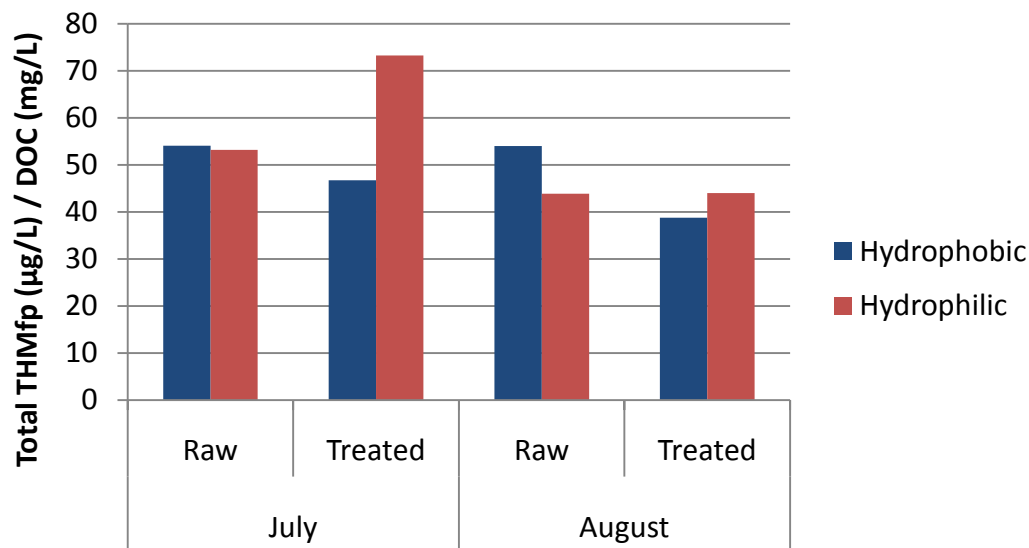
Figure 4.22 – Variation in the total THMfp of raw and treatment water organic fractions from the JDKWSP (plant conditions). Results are presented on a normalized yield basis.

Variations in the THMfp were further investigated by looking at the specific organic fraction formation potentials. The THMfp of the six organic fractions, in the raw and treated water, are presented in Figure 4.23. Results show the formation potential of fractions under uniform dosing and under plant dosing conditions. Under uniform dosing conditions, the hydrophobic acid fraction was the greatest contributor to THMfp in the raw water with a formation potential of approximately160 µg/L while the hydrophobic neutral fraction had the least THMfp with concentrations less than 10 µg/L. All other fractions appeared to have similar THMfp under uniform conditions. In contrast, the hydrophobic neutral fraction had the greatest formation potential (40 µg/L) under plant dosing conditions. The hydrophilic base fraction had the second greatest THMfp at 35 µg/L. All other fractions had formation potentials less than 10 µg/L. For all other months sampled, the contribution of each fraction to the total THMfp, under plant dosing conditions, was highly variable (Appendix C). The only consistency in THMfp was that the hydrophilic netural fraction had the lowest formation potential.

Similar formation potentials were observed for each fraction in the treated water with the exception that the hydrophobic and hydrophilic base fractions had the greatest formation potentials under plant dosing conditions.
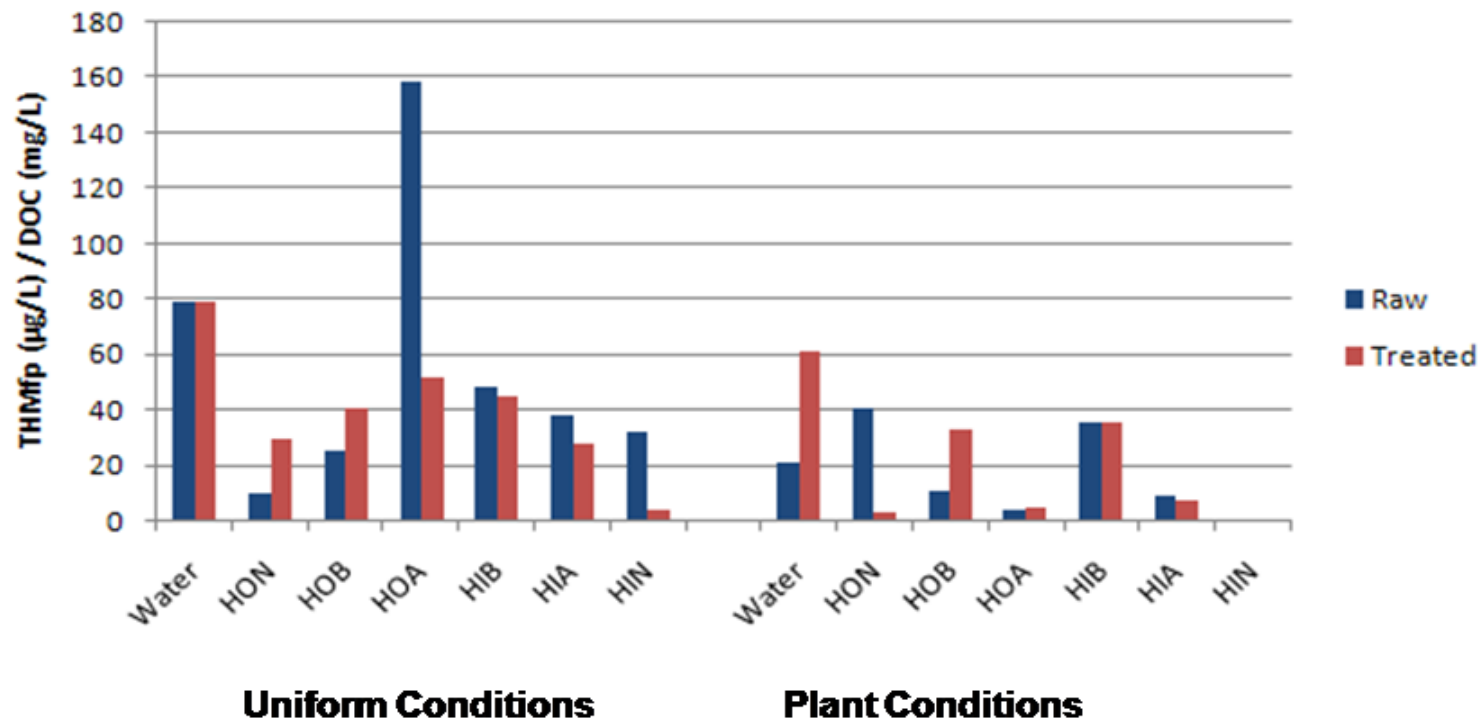
Figure 4.23 – Total trihalomethane formation potential of raw and filtered water organic fractions from the JDKWSP, sampled in August 2010. Results are presented on a normalized yield basis.

4.4.3. HAAfp of NOM at the JDKWSP

The total haloacetic acid formation potential (HAAfp) is reported in Figure 4.24. The total HAAfp was low (~25 µg/L) in the months of August 2009/2010 and July 2010. The highest HAAfp occurred in February 2010 where the concentration was 44 µg/L. Among the nine compounds evaluated, dichloroacetic acid had the highest formation potential with concentration between 3-18 µg/L. Bromoacetic acid and chloroacetic acid were also present in amounts between 3-8 µg/L in all sampling events except for July and August 2010. In these months the presence of bromoacetic acid and chloroacetic acid were not detected. Trichloroacetic acid was only present in July and August 2010 at concentrations of 4-5 µg/L. All other compounds tested were present in quantaties less than 1µg/L.
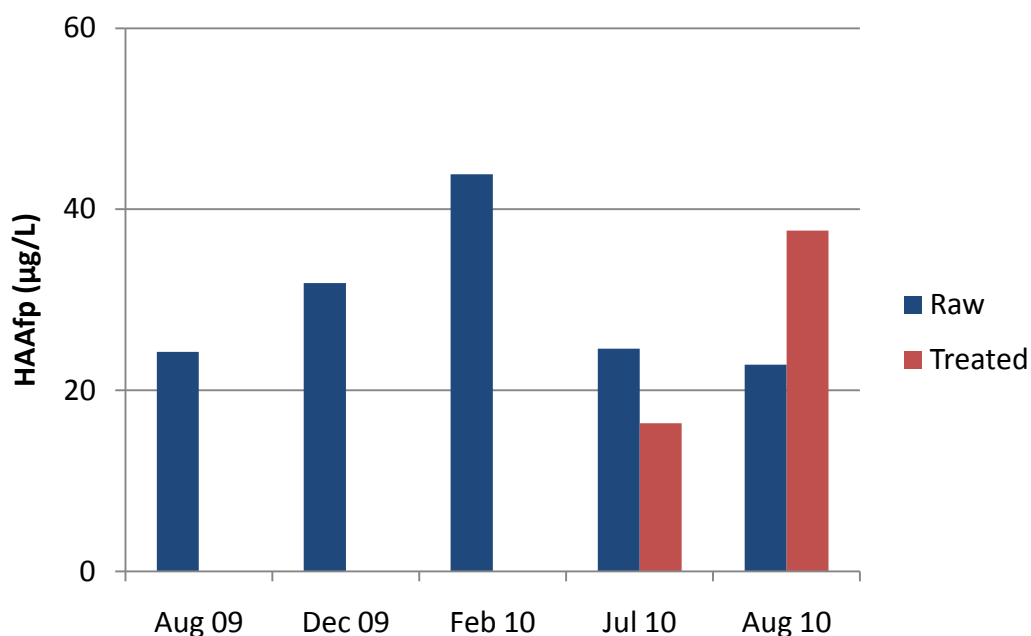
Figure 4.24 – Total haloacetic acid formation potential of raw and filtered water samples from the JDKWSP dosed under plant dosing condition.

4.4.4. HAAfp of Organic Fractions at the JDKWSP

The total HAAfp of raw and treated water hydrophobic and hydrophilic organic fractions are presented in Figure 4.25. These results describe the formation potential under plant dosing conditions. There were increases in the HAAfp of both fractions in the treated water. These increases were further investigated by looking at the specific organic fraction formation potentials (Figure 4.26).

The hydrophobic neutral and acid fractions had the highest HAAfp in the raw water under uniform dosing conditions while the hydrophobic base and hydrophilic neutral fractions had the least HAAfp. Similar trends among organic fractions were observed for the HAAfp of the treated water.

Under plant dosing conditions, the hydrophobic neutral and hydrophilic base fractions had the highest HAAfp. Under these conditions, the hydrophilic and hydrophobic acid fractions had the highest HAAfp in the treated water. For all other sampling events, the HAAfp of each fraction was highly variable (Appendix C). The hydrophilic neutral fraction, however, consistently contributed the least to the HAAfp.
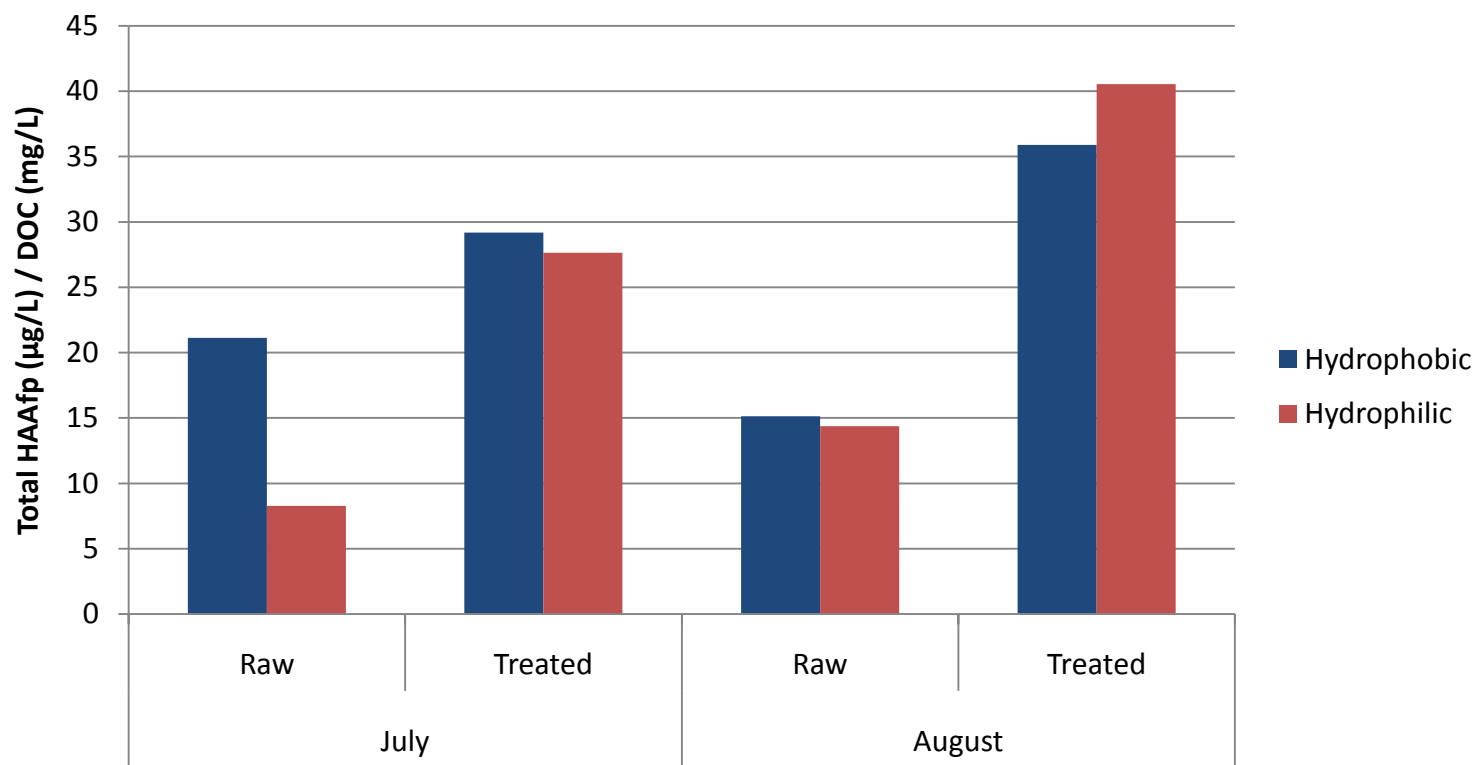
Figure 4.25 – Seasonal variation in the total HAAfp of raw and treatment water organic fractions from the JDKWSP. Results are presented on a normalized yield basis.
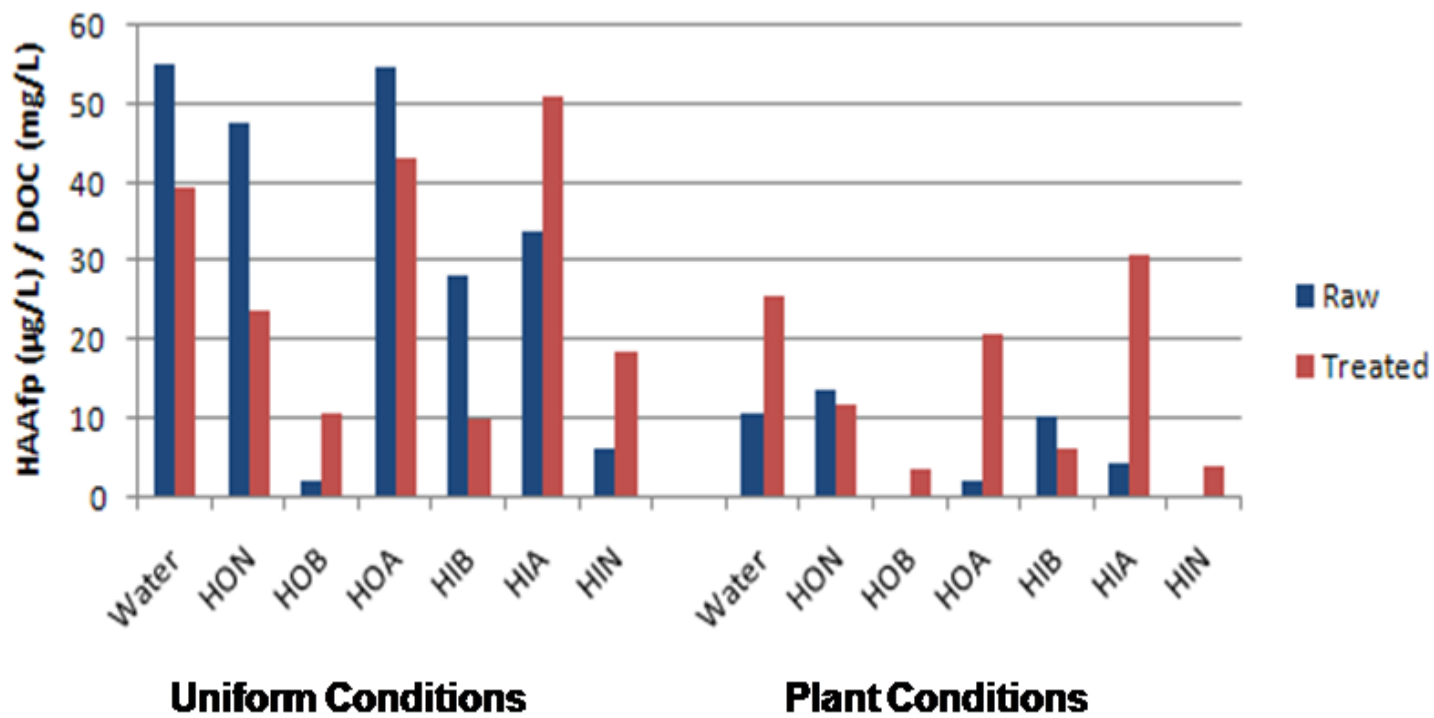
Figure 4.26 – Total haloacetic acid formation potential of raw and filtered water organic fractions from the JDKWSP, sampled in August 2010. Results are presented on a normalized yield basis.

4.4.5. THMfp of NOM at the MVWA

The total THMfp for raw and filtered water dosed under plant operating conditions are presented in Figure 4.27. The total THMfp for raw water was variable across sampling events (~60 – 121 µg/L). Chloroform was found to be the largest contributor to the total THMfp for each sampling event with concentrations between 53 – 116 µg/L. Bromodichloromethane was present in all samples in concentrations between 2.9 – 8.8 µg/L while dibromochloromethane was only present in May and October in concentrations less than 4µg/L. Bromoform was not present in any of the samples analyzed. The total THMfp of the treated water was also variable across sampling events, ranging between 52 – 86 µg/L. Despite the increase in THMfp in October in the raw water, there was little increase in the THMfp in the filtered water. Chloroform was again the largest contributor to the total THMfp in the treated water with concentrations ranging between 43 – 77 µg/L. Both dibromochloromethane and dichlorobromomethane were present in all samples in concentrations less than 10 µg/L while no bromoform was present.
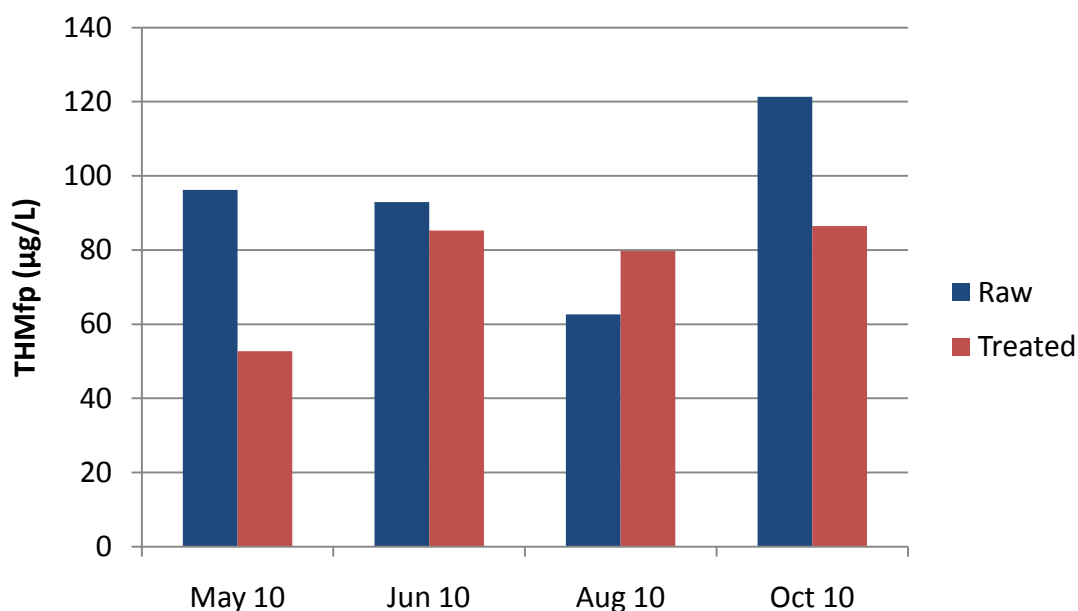
Figure 4.27 – Total trihalomethane formation potential of raw and filtered water samples from the MVWA dosed under plant dosing conditions.

4.4.6.   THMfp of Organic Fractions at the MVWA

The total THMfp of raw and treated water hydrophobic and hydrophilic organic fractions are presented in Figure 4.28.   Although the results described herein represent the formation potentials under plant dosing conditions similar trends were observed under uniform dosing conditions.

The THMfp in the raw water was highest in the hydrophobic fraction for the months of May and June. In contrast, higher THMfp were observed in the hydrophilic fraction of the raw water in August and October. In the treated water, the hydrophobic fraction had the highest THMfp for all months sampled.

The contribution of each of the six organic fractions was to the total THMfp of raw water and treated water are presented in Figure 4.29.   Under uniform conditions the hydrophobic acid fraction had the highest THMfp in the raw and treated water.   In contrast, this fraction contributed very little to the total THMfp under plant opreating conditions.   Under these conditions, the hydrophobic neutral and the hydrophilic base fractions were the greatest contributors to the total THMfp.

For all other sampling events, the THMfp of each fraction was highly variable (Appendix C). The hydrophilic neutral fraction, however, consistently contributed the least to the THMfp in both the raw and treated water samples.
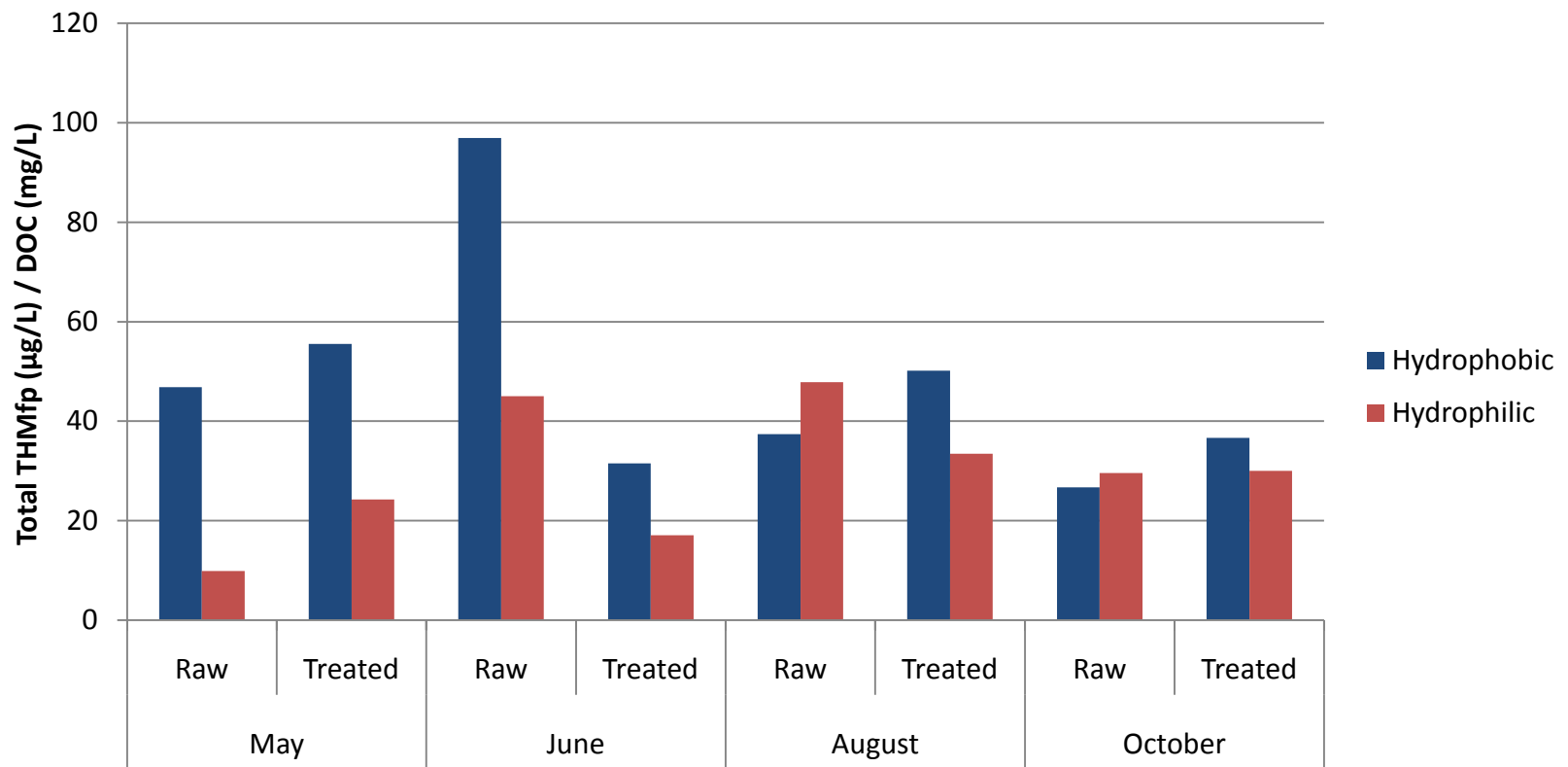
Figure 4.28 – Seasonal variation in the total THMfp of raw and treatment water organic fractions from the MVWA. Results are presented on a normalized yield basis.
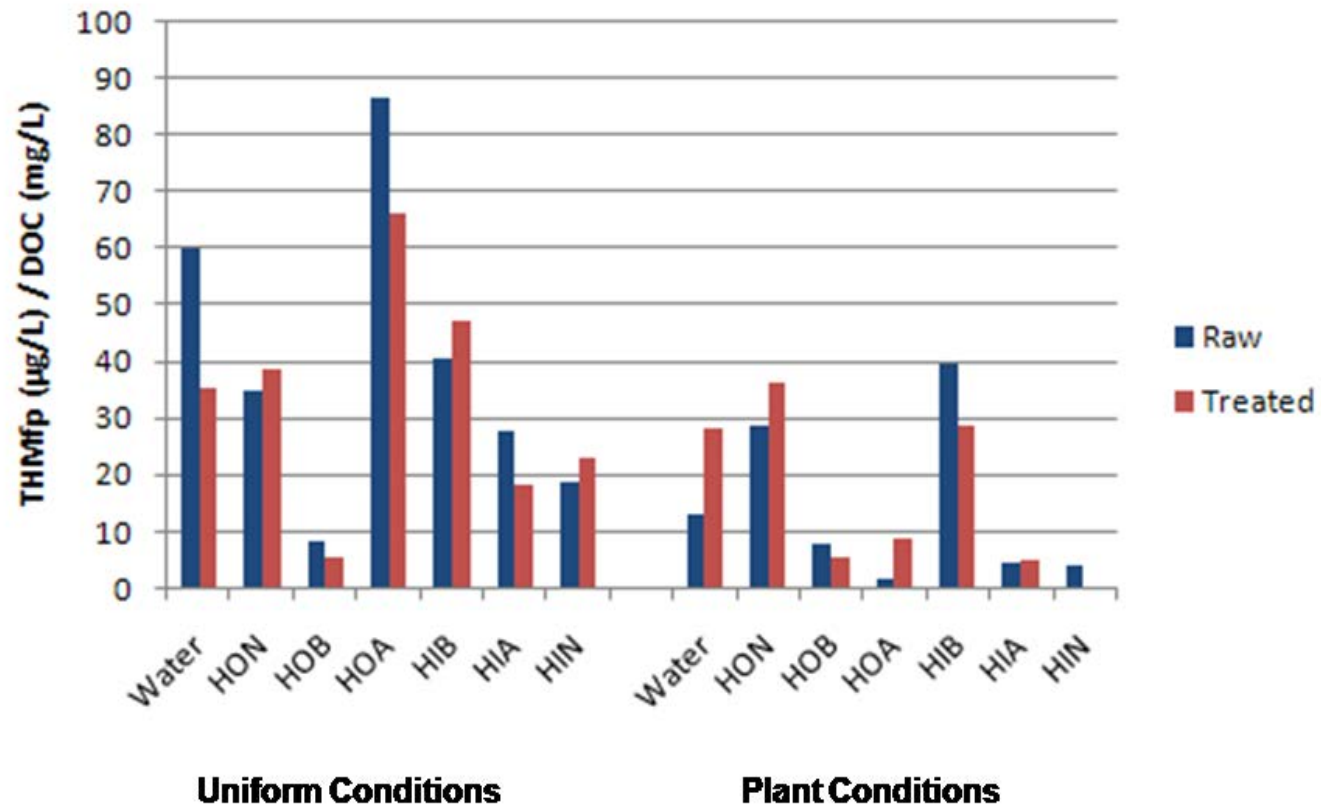
Figure 4.29 – Total trihalomethane formation potential of raw and filtered water organic fractions from the MVWA, sampled in August 2010. Results are presented on a normalized yield basis.

4.4.7.   HAAfp of NOM at the MVWA

The total HAAfp for the raw and treated water dosed under plant operating conditions are presented in Figure 4.30. May and October saw the highest HAAfp in the raw water with concentrations of 111 μg/L and 106 μg/L respectively. The lowest HAAfp in the raw water was reported in August with a concentration of 45 μg/L.   Among the nine compounds tested, dichloroacetic acid and trichloroacetic acid were the greatest contributors to the total HAAfp in the raw and treated water with concentrations between 20 – 49 μg/L and 14 – 52 μg/L respectively. All other compounds were present in quantities of less than 12 μg/L.
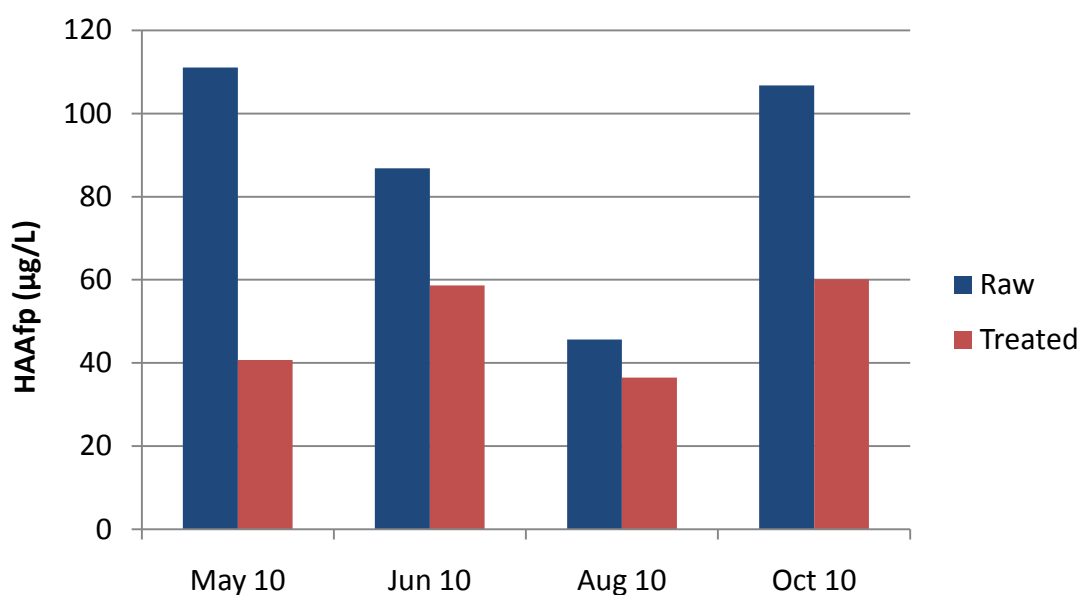
Figure 4.30 – Total haloacetic acid formation potential of raw and filtered water samples from the MVWA dosed under plant dosing conditions.

4.4.8. HAAfp of Organic Fractions at the MVWA

The total THMfp of raw and treated water hydrophobic and hydrophilic organic fractions are presented in Figure 4.31. These results describe the formation potential under plant dosing conditions. The hydrophobic fraction had the greatest HAAfp in both the raw and treated water except in the month of October, where the hydrophilic fraction contributed most to HAAs in the treated water. Similar trends were observed under uniform dosing conditions.

The HAAfp of the six organic fractions, for raw and treated water, are presented in Figure 4.32. The hydrophobic acid fraction had the highest HAAfp in the raw water under uniform dosing conditions while it contributed very little to the HAAfp under plant dosing conditions. The hydrophobic base and hydrophilic neutral fractions had the least HAAfp in the raw and treated water under both dosing conditions. Under plant dosing conditions, the hydrophobic neutral and hydrophilic base fractions had the highest HAAfp.

As with the THMfp, the HAAfp of each fraction was highly variable for all sampling events (Appendix C). The hydrophilic neutral fraction, however, consistently contributed the least to the HAAfp in both the raw and treated water samples.
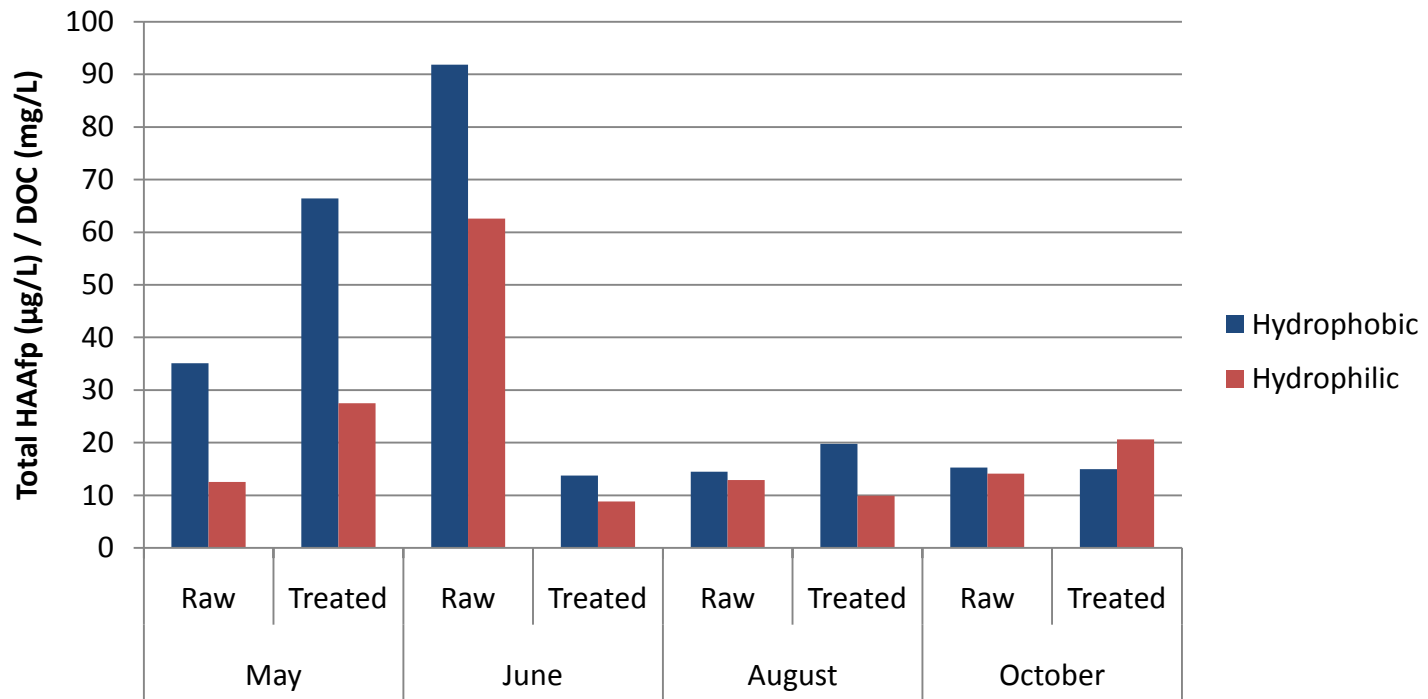
Figure 4.31 – Seasonal variation in the total HAAfp of raw and treatment water organic fractions from the MVWA. Results are presented on a normalized yield basis.
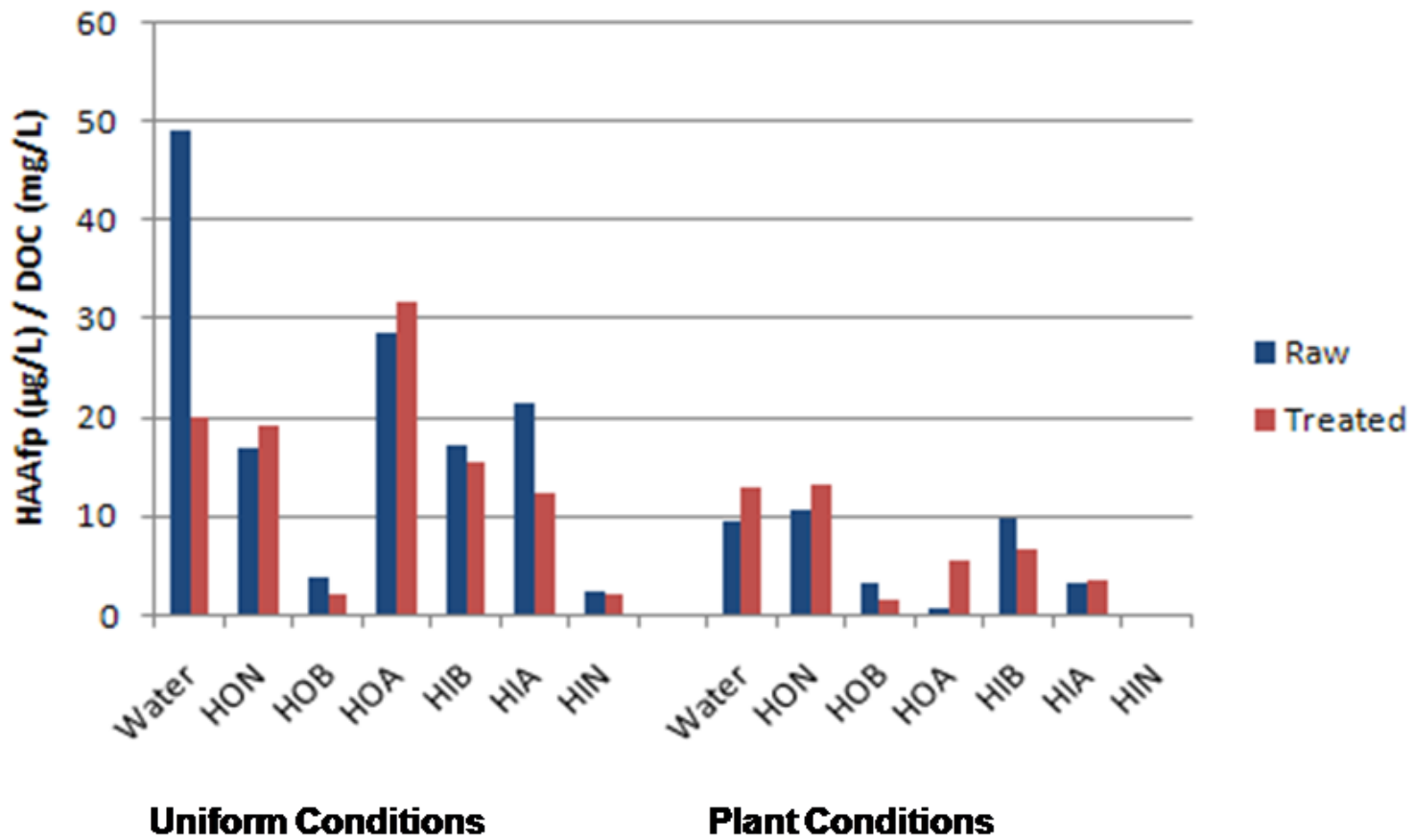
Figure 4.32 – Total haloacetic acid formation potential of raw and filtered water organic fractions from the MVWA, sampled in August 2009. Results are presented on a normalized yield basis.

4.5.   Comparison of Raw Water Characteristics Between Watersheds

Table 4.3 summarizes the characteristics observed from the raw water organic fractions sampled from the JDKWSP and the MVWA. The values in the table represent the lower and upper range of values obtained from each analysis. Values for the THMfp and HAAfp represent those obtained for samples dosed under plant operating conditions.

Resin fractionation showed that the organic composition varied between and within each watershed. In particular, there was much more variation in the composition of the organic matter matrix in the JDKWSP raw water samples. The most abundant fraction was typically the hydrophilic neutral, however the second and third most abundant fractions varied between sampling events. Raw water samples analyzed from the MVWA showed the hydrophilic neutral and the hydrophobic acid fractions as being the most abundant in the watershed with each sampling event.

Size exclusion chromatography analysis showed that the molecular weight ranges of organic fractions did not vary between water sources except for the hydrophobic acid and neutral fractions. The hydrophobic acid fraction from the MVWA was comprised of compounds in the range of 59400 – 35 Da compared to compounds from the JDKWSP whose molecular weight range was 1100 – 90 Da. In contrast, the largest compounds at the JDKWSP were hydrophobic neutral in nature and whose molecular weights ranged between 60600 – 80 Da. This fraction from the MVWA comprised smaller compounds in the range of 1450 – 100 Da.

The zeta potential analysis of organic fractions showed very similar results between watersheds. The pH where fractions approached charge neutrality (between - 5 to +5 mV) was typically below a pH of 2.5 for all fractions except the hydrophobic neutral fractions which did not reach a point of charge neutrality over the pH range evaluated. The hydrophobic base fraction from both watersheds showed remarkable similarity in their zeta potential. The only observed difference in zeta potentials was seen between the hydrophlic neutral fractions of either watershed. Charge neutrality was achieved at pH values of less than 2.5, 7 and 8.6 for the MVWA sample. In comparison, charge neutrality was only reached at a pH < 2.5 for the JDKWSP.

The DBP analysis of samples from the two watersheds also showed similarities in the formation potential of each organic fraction.

Table 4.3 – Summary of results from the raw water characterization of samples taken from the JDKWSP and the MVWA.

	Organic Fraction	% Composition	Mw Range (Da)	pH of Charge Neutrality	THMfp (μg/L)	HAAfp (μg/L)
JDKWSP	RAW	-	56000 - 80	< 2.5	10 - 21	10 -21
MVWA	RAW	-	61500 - 100	< 2	13 - 27	9 - 30
JDKWSP	HON	1 - 41	60600 - 80	-	13 - 40	4 - 14
MVWA	HON	0.6 - 6	1450 - 100	-	14 - 28	10 - 56
JDKWSP	HOB	0.4 - 30	1050 - 85	2 – 6, 10	3 - 43	0 - 7
MVWA	HOB	1 - 4	1100 - 110	2 – 6, 10	0.7 - 72	3 - 30
JDKWSP	HOA	4 - 31	1100 - 80	< 2.5	2 - 11	2 - 7
MVWA	HOA	20 - 64	59400 - 35	< 2.5	1 - 3	0.7 - 5
JDKWSP	HIB	1 - 46	1100 - 90	< 2.5	2 - 35	2 - 10
MVWA	HIB	0.7 - 6	1100 - 45	< 2.5	1 - 40	1 - 10
JDKWSP	HIA	0.1 - 25	1100 - 90	< 2	6 - 33	4 - 31
MVWA	HIA	1 - 42	1200 - 115	< 2	0.9 - 42	1 - 44
JDKWSP	HIN	16 - 59	1100 - 85	< 2.5	0 - 9	0 - 1
MVWA	HIN	22 - 53	815 - 100	< 2.5, 7, 8.6	2 - 4	0 -13

CHAPTER 5   DISCUSSION

5.1   NOM Characterization

5.1.1   Resin Fractionation

The resin fractionation procedure proposed by Marhaba *et al.* (2003) was chosen for the characterization of NOM in this research. This procedure offered the separation of organics into six classes and was intended specifically to characterize source waters containing low DOC making it a suitable choice for the characterization of raw and treated water from both the MVWA and the JDKWSP. The DOC recovery, using resin fractionation with XAD-8 and XAD-4, was estimated at 60 – 80% (Croue *et al.,* 2000). While the overall recovery of DOC using DAX-8, AG-MP 50 and WA-10 ion exchange resins was not reported, it is reasonable to expect some loss.

The difference in DOC between columns and analysis of the DOC from the column extracts have both been used to quantify the DOC of fractions (Marhaba *et al.,* 2003; Imai *et al.,* 2001). Where the concentration of DOC of a fraction is expected to be below 0.20 mg/L, the quantification of DOC based on column differences is preferred (Marhaba *et al.,* 2003).   In the case of samples analyzed from the JDKWSP and the MVWA, sample volumes of 20 L were fractionated, thus producing organic fraction concentrates well above the 0.20 mg/L suggested. The use of both quantification methods, in this study, was therefore deemed acceptable.

The sum of DOC recovered from each fraction was sometimes greater than the DOC of the raw water sample indicating an increase in mass during the fractionation procedure. This was attributed to DOC bleed from the resins following cleaning and verified by measuring the DOC of the column effluents prior to passing samples through the columns. This occurrence was also reported by Marhaba *et al.* (2003), Kanokkantapong *et al.* (2006) and Leenheer (1981) who found that DOC from clean resins to be as high as 0.3 mg/L.

5.1.2 Seasonal Variation in the NOM Composition

The organic composition of the raw water from the JDKWSP and the MVWA was variable between and within watersheds. In both watersheds, however, the hydrophilic neutral fraction was one of the most abundant. This was also found to be the case in sources investigated by Marhaba *et al.* (2003), Kanokkantapong *et al.* (2005, 2006) using the same fractionation procedure.

In October, the DOC of raw water samples increased by ~ 3 mg/L and ~ 1 mg/L above the average at the MVWA and the JDKWSP respectively. Fractionation results showed that this increase was primarily an increase in the hydrophobic acid content at the MVWA and an increase in the hydrophilic base content at the JDKWSP. Although no formal correlation studies between DOC composition and rainfall were conducted in this study, it was reported that significant precipitation and flooding had occurred prior to the sampling of the MVWA watershed in October. Similar studies have reported that increases in DOC resulting from increased precipitation were attributed to increases in the humic component of the hydrophobic acid fraction (Sharp *et al.,* 2005; Malcolm, 1985). The increase in the hydrophilic base fraction, in the JDKWSP raw water sample, in the fall, by contrast, has not been reported and further validates the necessity to characterize the NOM of each watershed to identify potential trends due to seasonal variation.

In addition to precipitation, differences in topography, climate and anthropogenic influences on watersheds can affect the NOM composition (Gjessing, 2003). While these differences and their affects are beyond the scope of this research, they are important considerations to keep in mind when comparing source water quality in different watersheds.

5.2   NOM Removal

A comparison of DOC results between the raw and treated water samples from the JDKWSP revealed that only 25% and 28% of DOC was removed during the months of July and August, 2010, respectively. Integration of the area under the SEC elution curves further revealed that removal of refractive organic compounds was between 50 to 53%. In comparison, NOM removal was much greater at the MVWA. DOC results from the raw and treated samples revealed removal rates of 49 to 70% over the sampling period. MVWA SEC results showed, on average, a 74% removal of refractive organics. Improved NOM removal rates observed at the MVWA were likely due to the abundance of the hydrophobic acid fraction in the raw water. SEC results have shown this fraction to be comprised of compounds whose molecular weights ranged between 60,000 – 120 Da, the largest of which were removed during treatment.   When the DOC of the hydrophobic fraction increased substantially in the raw in October, the treated water DOC remained within normal ranges.

Removal of NOM at the JDKWSP was primarily a removal of the hydrophobic acid and the hydrophilic neutral fractions with little to no removal of other fractions. The smaller DOC removal rates observed at the JDKWSP were likely due to the lower hydrophobic acid content of the raw water.

5.2.1 Coagulant Interactions with the Hydrophobic Fractions

Numerous studies have shown the hydrophobic fractions to be more readily removed during coagulation than other fractions (Sharp *et al.,* 2006; Edzwald, 1993; Ratnaweera *et al.,* 1999). Certain chemical and physical properties exhibited by these fractions have been found to be preferential in their reaction with coagulants such as alum. Several studies have shown that the hydrophobic acid fraction, in particular, has a large charge density and that this promotes its interactions with coagulants (Sharp *et al.,* 2006; Edzwald, 1993; Collins *et al.,* 1986). Additional studies have shown a correlation between molecular weight and charge density such that larger compounds have a greater

charge density (Ratnaweera *et al.,* 1999). As well, the larger the negative surface charge, the greater the interaction with the positively charge metal oxidants (Ratnaweera *et al.,* 1999).

Among fractions, the greatest percentage of DOC removal occurred within the hydrophobic acid fraction at both treatment plants. Preliminary zeta potential analysis of organic fractions, from this study, suggest that the colloidal charge in the raw water was driven by the hydrophobic fractions as opposed to the hydrophilic fractions. In particular, the hydrophobic acid fraction had very similar zeta potentials as the raw water from both watersheds between a pH range of 2 to7. At the operational coagulation pH of 5.5 at the JDKWSP, the hydrophobic acid fraction and raw water had zeta potentials of -17 mV. In comparison, the zeta potential of the raw water and the hydrophobic acid fraction at the MVWA was -20 mV at an operational coagulation pH of 5.9. As expected, the negative surface charge of organics within this fraction was correlated with increased removal rates.

Removal of DOC from the hydrophobic neutral fraction was small within both treatment plants. Removal of the largest of these compounds at the JDKWSP translated into little DOC removal. The low charge density exhibited by small compounds might offer a possible explanation for the low removal rates of this fraction; however, this variable was not specifically evaluated in this study. The zeta potential results for this fraction indicate a desirable surface charge of -25 mV at operational coagulation pH, suggesting it should be removed during treatment. Further investigations into the interaction of this fraction and alum would be warranted given its abundance in the JDKWSP raw water and its high contribution to DBPfp.

There was little to no removal of DOC from the hydrophobic base fraction at either treatment plants. This is most likely related to the positive surface charge exhibited by this fraction at operational coagulation pH. Additionally, SEC results have shown this fraction to be comprised of smaller compounds which have been associated with a low charge density (Ratnaweera *et al.,* 1999).

5.2.2   Coagulant Interactions with the Hydrophillic Fractions

The DOC of the hydrophilic organic fraction in the raw water has often been used to predict the residual DOC in the treated water as this fraction is believed to interact little with alum during coagulation (White *et al*., 1997; Edzwald, 1993). A study by Sharp *et al.* (2006) revealed that the hydrophilic fraction contributed to only 11% of the total charge load of the raw water. Furthermore, it was found that the hydrophilic frations had a very low charge density of less than 1.0 meqg^{-1}, suggesting that most of the coagulant demand could be predicted from the hydrophobic content of the raw water (Sharp *et al.,* 2006; Edzwald, 1993). White et al. (1997) noted that the removal of hydrophilic compounds was likely to occur only when the coagulant demand of the hydrophobic compounds was satisfied.

DOC results from this study have found that a substantial portion of the hydrophilic neutral fraction was removed during treatment. At the JDKWSP, the DOC removal of this fraction was 40% in the month of July and 48% in the month of August. Removal of this fraction was much more variable at the MVWA where increases in this fraction were observed in the treated water during some sampling events, while others have shown DOC removals of up to 70%.

Despite the low charge densities of these fractions reported in previous studies and low molecular weights reported in this study, there appears to be another factor promoting the removal of DOC from this fraction. Zeta potential analysis reveals that the hydrophilic neutral fraction had a surface charge of -12 to -10 mV over the pH range for coagulation at the JDKWSP. Similarly, the zeta potential of this fraction in MVWA samples under at a coagulating pH of 5.9 was -15 mV. This negative surface charge may have promoted its interaction with alum.

5.2.4   Changes in DOC Composition

In addition to the removal of DOC within particular organic fractions after coagulation and filtration, increases in DOC were also observed. This was most noticeable within the DOC results for the hydrophilic base fraction (Appendix A). SEC results, showed the presence of small compounds, indicated by peak 10, in the treated water. These results suggest that, during coagulation and filtration, smaller compounds are being formed. Further, these compounds are exhibiting different chemical properties than their ―parent‖ compound. This is explained by the fact that compounds within a particular fraction are formed from smaller aliphatic and amphiphillic molecules (Croue *et al.,* 2000).

5.2.5   Operational Considerations

Several differences in the operational treatment of water between the JDKWSP and the MVWA could explain differences in the DOC removal observed between plants. The JDKWSP coagulates at a dose of 8 mg/L and a pH of 5.5 throughout the year.   In comparison, coagulation at the MVWA is much more variable depending on the raw water quality. Alum doses in this study ranged between 17 to 30 mg/L at pH 5 to 6.3. These flexible coagulation conditions likely enable the MVWA to achieve a greater DOC removal, in spite of significant increases in NOM in the raw water.

Another major difference in the two treatment plants is the type of mixing used during the coagulation/flocculation process. The MVWA employs mechanical mixing while the JDKWSP relies on hydraulic mixing. While a case can be made for the benefits of each type of mixing, hydraulic mixing tends to be less flexible in its operation (Haarhoff and van der Walt, 2001). Without proper design of the flocculation tanks, the energy input, for mixing, tends to vary based on the flow rates (Haarhoff and van der Walt, 2001). This translate to a lesser degree of control over the promotion of floc formation in the flocculation tanks. As well, computational flow dynamic modelling of the flocculation tanks in the JDKWSP have shown regions where little to no mixing is occurring

(Vadasarukkai, 2010). This might also offer an explanation to the decreased NOM removal rates observed at the JDKWSP.

5.3   Disinfection By-Product Formation Potential

5.3.1   Seasonal Variation in DBPfp

The DBPfp of the raw water from both watersheds varied between sampling events. In general, there appeared to be a greater DBPfp starting in the late fall and following through to the winter months. This coincided with increases in DOC in the source water. Chen *et al.* (2008) reported similar findings, where the highest THMfp occurred in September and in December and the lowest formation potentials were observed in March and July. Although microbiotic communities are most active in the summer, much of the dissolved organic matter produced remains trapped in the soil (Scott *et al,.* 2001). The release of this organic matter into the water column usually coincides with increased precipitation observed in the fall. High DBPfp, observed in the winter, has been thought to arise from the delayed decaying of biomass accumulated in the fall (Scott *et al*., 2001).

Additionally, raw water samples from the MVWA showed an increased DBPfp in May. This did not coincide with an overall increase in DOC, but rather an increase in the hydrophilic acid fraction. This fraction was found to be an important contributor to DBPs, under uniform dosing conditions.

5.3.2   DBPfp of Organic Fractions

The DBPfp was much higher for samples dosed under uniform conditions than those dosed under plant operating conditions. This was explained by the differences in chlorine dosing between the two conditions. Under uniform conditions, the chlorine dosage was variable between fractions to ensure a residual of 1 ± 0.4 mg/L after a 24 hour incubation

period. This dosage ranged between 8 to 20 mg/L. Under plant operating conditions these dosages were much lower; 1 mg/L at the JDKWSP and 2.5 mg/L at the MVWA. While the total formation potentials under the two conditions were different, the overall formation potential trends were similar between fractions. The hydrophobic acid fraction, however, was an exception to the observed trend. Under uniform conditions, the hydrophobic acid fraction from both watersheds contributed most to DBPs. Similar studies have also shown this fraction to be an important DBP precursor (Marhaba and Van, 1999; Marhaba and Van, 2000; Croue et al., 2000; Chang et al., 2001). In contrast, this fraction contributed very little to the DBPfp under plant dosing conditions. While the reaction kinetics for this particular fraction to form DBPs is not understood, these results suggest that a high chlorine dosage is required before the hydrophobic acid fraction becomes an important DBP precursor.

The hydrophilic neutral fraction contributed very little to the DBPfp in both raw and treated water, on a normalized yield basis. Low to moderate DBPfp resulting from this fraction, on a normalized yield basis, was also reported by Marhaba and Van (1999 and 2000) and Croue et al. (2000). On a mass basis, however, the hydrophilic neutral was an imporant THM precursor in both the raw and treated water for both plants. The THMfp of this fraction was variable throughout sampling events. The degree of reactivity of this fraction was thought to be related to the polysaccharide content; increased polyssaccharide content has been shown to result in decreased reactivity with chlorine (Bruchet et al., 1987).

Under both uniform and plant dosing conditions, the raw water hydrophobic neutral and the hydrophilic acid fractions of both watersheds had high DBPfp. With respect to the HAAfp, these fractions contributed most. There are conflicting findings as to the DBPfp of these fractions. Marhaba and Van (1999 and 2000), Croue et al. (2000) and Kanokkantapong et al. (2006) have found that the hydrophobic neutral fraction had moderate to high HAAfp. In contrast, Chen et al. (2008) and Chang et al. (2001) have found this fraction to have a low HAAfp and THMfp. Similarly, the hydrophilic acid fraction's role as a DBP precusor is also dubious. Marhaba and Van (1999 and 2000) and

Chen *et al.* (2008) have found this fraction to have low to moderate DBPfp while Croue *et al.* (2000) found this fraction to be the greatest contributor to HAAs.

The disagreement in the literature, pertaining to the formation potentials of organic fractions, is evidence that the specific organic compounds comprised within each organic fraction vary between water sources (Kanokkantapong *et al.,* 2006). Therefore, optimization of DOC removal, for the purpose of mitigating DBPs, requires specific knowledge of the types and quantities of organic fractions and their reactivites to chlorine.

5.3.3   DBPfp and Chlorine Dosing Conditions

Two different chlorine dosing conditions were investigated in this study; uniform dosing conditions and plant dosing conditions. Uniform dosing conditions allowed the determination of formation potentials without chlorine being a limiting factor. Consequently, the formation potentials of organic fractions, under these conditions, were higher. Under plant dosing conditions, however, chlorine dosing was limited to 1 mg/L for the JDKWSP samples and 2.5 mg/L for the MVWA samples. After a 24 hour incubation period, there was often no residual chlorine. As a result, the DBPfp of fractions under these conditions were lower.

Trends in the formation of DBPs among fractions were comparable between the two dosing conditions for all fractions except for the hydrophobic fraction. This fraction was the greatest contributor to DBPs under uniform dosing conditions. In contrast, it contributed very little to DBPs under plant dosing conditions. These results suggest that higher chlorine doses might be required before this fraction becomes an important DBP contributor.

Another difference between dosing conditions was observed in the formation potentials of the raw and treated water. Under plant dosing conditions, the raw water DBPfp was lower than that of the treated water for many of the sampling events. A possible explanation for this occurrence is the presence of a greater concentration of inorganic

compounds in the raw water. Singer (2008) estimated the chlorine demand of iron and manganese to be 0.64 mg/L and 0.93 mg/L per mg/L of chlorine, respectively. As well, inorganic compounds have been shown to react quickly with chlorine compared to organic compounds (Deborde and von Guten, 2008). Under plant dosing conditions, a large portion of the chlorine likely reacted withinorganic compounds present in the raw water. This would result in less free chlorine available for subsequent DBP formation reactions. In contrast, lower inorganic concentrations, typically present in treated water, would result in greater chlorine availability for reactions with organic compounds.

CHAPTER 6   CONCLUSIONS & RECOMMENDATIONS

6.1   Conclusions

Natural organic matter characterization of raw water was conducted on two watersheds; one supplying the JDKWSP and the other supplying the MVWA. In spite of similarities in the raw water characteristics between the two different watersheds, their NOM composition was highly variable between and within each source. The raw water of the JDKWSP was primarily comprised of hydrophobic and hydrophilic neutral compounds while the raw water of the MVWA was primarily comprised of hydrophobic acid and hydrophilic neutral compounds. The molecular weight ranges of most organic fractions were approximately 1100 to 65 Da, for both plants, such that distinctions based on size could not be made. The largest compounds in the raw water however could be distinguished as hydrophobic acid compounds in the raw water of the MVWA and hydrophobic neutral compounds in the raw water of the JDKWSP. Zeta potential analysis of individual fractions revealed an overall negative surface charge for all fractions except for the hydrophobic base and hydrophilic neutral fractions. The hydrophobic base fractions exhibited a positive surface charge between pH of 2 to 3 and approximately5 to 10. Similarly, the hydrophilic neutral fraction from the MVWA had a positive surface charge between pH 7.0 to 8.7.

The disinfection by-product formation potential of individual fractions was subsequently evaluated to determine which types of organics contributed most to THMs and HAAs in the raw water. On a normalized yield basis, the hydrophobic acid fraction was the greatest contributor to both the THMfp and HAAfp under uniform dosing conditions. This fraction, however, contributed very little to DBPs under plant dosing conditions. On a mass basis, this fraction was an important contributor to the formation of DBPs in the raw and treated water of the MVWA.

The hydrophobic neutral and hydrophilic acid fractions were also found to be important DBP precursors in both watersheds, on a normalized yield basis. On a mass basis, their contribution to DBPs was variable between sampling events.

Finally, the hydrophilic neutral fraction contributed little to DBPs under both uniform and plant dosing conditions, on a normalized yield basis. On a mass basis, however, this fraction was an important contributor to the THMfp.

The removal of organic fractions was subsequently evaluated. The JDKWSP experienced lower DOC removal rates than the MVWA. These differences were primarily attributed to the abundance of the hydrophobic acid fraction in the raw water of the MVWA and its preferential removal by alum. While DOC removal among the remaining fractions was similar between treatment plants, the JDKWSP achieved a greater removal of DOC from the hydrophilic neutral fraction. In contrast, there was little to no removal of the hydrophobic base fraction at either treatment plant. This was attributed to the positive surface charge exhibited by this fraction at coagulation pH ranges evaluated in this study.

6.2   Recommendations

Based on the preliminary findings of this study, several recommendations with regards to the direction of NOM characterization can be made. Continued characterization using resin fractionation should be carried out on raw and treated water samples. This would be particularly useful for the JDKWSP, where only two treated water samples were characterized.

Following fractionation, additional studies should be carried out on the concentrated fractions. The UV_{254} and color contribution of each fraction should be determined to see if correlations can be made between raw water quality and the organic composition. Analysis of the zeta potential of fractions should be continued to try to determine a link between the zeta potential of fractions and their removal. This might help direct the optimization of coagulation conditions for the removal of organic fractions most responsible for increased DOC and DBPfp. As well, charge density studies should be

conducted to help determine which chemical characteristics are most important for improved interaction with coagulants.

Futher DBP analyses should be performed on the raw and treated water fractions under different incubation periods and dosages to further investigate the reaction kinetics of particular organic fractions. More specifically, a longer incubation period simulating residence time in a distribution system to reflect the DBPfp of fractions representative at regulatory sampling locations.

Bench scale coagulation studies simulating plant conditions should also be carried out on each of the raw water fractions to determine the removal rates between fractions. Additional coagulants should be investigated to optimize DOC removal to those fractions identified as important DBP precursors at the JDKWSP and the MVWA. Studies exploring other treatment options might be required in order to achieved further reductions in DBPs.

REFERENCES

APHA. (1995) Standard methods for the examination of water and waste water, 19th Edition. *American Public Health Association; American Water Works Association and the Water Environment Federation*, USA.

Bove, F.J., Fulcomer, M.C., Klotz, J.B., Esmart, J., Dufficy, E.M., and Savrin, J.E. (1995) Public Drinking Water Contamination And Birth Out-Comes. *American Journal of Epidemiology,* **141**: 850-862.

Bruchet, A., Anselme, C., Marsigny, O. and Mallevialle, J. (1987) THM formation potential and organic content: A new analytical approach. *Aqua,* **2**: 102-109.

Chang, C.U., Hsieh, Y.H., Lin, L., Hu, P.Y., Liu, C.C. and Wang, K.H. (2001) The organic precursors and their relationship with disinfection by-products. *Chemosphere,* **44**: 1231-1236.

Chen, B., Westerhoff, P. and Krasner, S.W. (2008) Fate and transport of wastewater-derived disinfection By-Products in surface waters. *Disinfection By-Products in Drinking Water: Occurrence, Formation, Health Effects, and Control*. Washington, USA.

Chisholm, K., Cook, A., Bower, C., and Weinstein, P. (2008) Risk of birth defects in Australian communities with high levels of brominated disinfections by-products. *Environmental Health Perspectives*, **116**: 1267-1273.

Collins, M.R., Amy, G.L. and Steelink, C. (1986) Molecular weight distribution, carboxylic acidity, and humic substances content of aquatic organic matter. Implications for removal during water treatment. *Environmental Science and Technology*, **20**: 1026-1032.

Croue, J.P., Korshin, G.V., and Benjamin, M. (2000) Characterization of Natural Organic Matter in Drinking Water. *AWWA Research Foundation and AWWA Association.*

Deborde, M and von Gunten, U. (2008) Reactions of chlorine with inorganic and organic compounds during water treatment – Kinetics and mechanisms: A critical review. *Water Research*, **42**: 13-51.

Dobbs, R.H., Wise, R.H. and Dean, R.B. (1972) The use of u.v. absorbance for monitoring the total organic carbon content of water and wastewater. *Water Research,* **6**: 1173–1180.

Dodds, L., King, W., Allen, A.C., Armson, B.A., Fell, D.B. and Nimrod, C. (2004) Trihalomethanes in public water supplies and risk of stillbirth. *Epidemiology*, **15**: 179-186.

Edwards, M. (1997) Predicting DOC removal during enhanced coagulation. *Journal of the American Water Works Association,* **89**: 78-89.

Edzwald, J.K. (1993) Coagulation in drinking water treatment: Particles, organics and coagulants. *Water Science and Technology,* **27**: 21-35.

Edzwald, J.K. (1994) Coagulation: Applications, basics and concepts of TOC removal. *Enhanced Coagulation Research Workshop, Dec 4-6*, Charleston, North Carolina.

Fearing, D.A., Banks, J., Wilson, D., Hillis, P.H., Campbell, A.T. and Parsons, S.A. (2004) NOM control options: The next generation. *Water Science Technology: Water Supply*, **4**: 139-45.

Gjessing, E.T. (2003) Short term and long term changes and variation in quality. *Workshop on Changes in Quality and Quantity of dissolved NOM; Causes and Consequences*, Atna 21-23 May 2003. In NT Technical Report available at: http://www.nordtest.org/register/techn/tclickon.htm

Gu, B., Schmitt, J., Chen. Z., Liang, L. and McCarthy, J. (1995) Adsorption and desorption of different organic matter fractions on iron oxide. *Environmental Science and Technology*, **59**: 219-229.

Harhoff, J. and van der Walt, J.J. (2001) Towards optimal design parameters for around-the-end hydraulic flocculators. *Journal of Water Supply: Research and Technology – Aqua*, **50.3**: 149-159.

Health Canada. (2006) Guidelines for Canadian Drinking Water Quality: Guideline Technical Document — Trihalomethanes. *Water Quality and Health Bureau, Healthy Environments and Consumer Safety Branch*, Ottawa, Canada.

Health Canada. (2008) Guidelines for Canadian Drinking Water Quality: Guideline Technical Document — Haloacetic Acids. *Water, Air and Climate Change Bureau, Healthy Environments and Consumer Safety Branch,* Ottawa, Canada.

Hildesheim, M.E., Cantor, K.P., Lynch, C.F., Dosemeci, M., Lubin, J., Alavanja, M. and Craun, G.F. (1998) Drinking water source and chlorination byproducts in Iowa. II: Risk of colon and rectal cancers. *Epidemiology,* **9**: 29-35.

Hodgeson, J.W. and Cohen, A.L. (1990) Determination of chlorination disinfection byproducts, chlorinated solvents, and halogenated pesticides/herbicides in drinking water by liquid-liquid extraction and gas chromatography with electron capture detection. *Environmental Protection Agency*, Cincinnati, USA.

Hongve, D., Rise. G., and Kristiansen, J.F. (2004) Increased color and organic acid concentrations in Norwegian forest lakes and drinking water – a result of increased precipitation? *Aquatic Sciences – Research Across Boundaries*, **66**: 231-238.

Huang, C. and Shiu, H. (1996) Interactions between alum and organics in coagulation. *Colloids and Surfaces A*, **113**: 155-163.

Imai, A., Fukushima, T., Matsushige, K., and Kim,Y.H. (2001) Fractionation and characterization of dissolved organic matter in a shallow eutrophic lake, its inflowing rivers, and other organic matter sources. *Water Resources,* **35**: 4019-4028.

Kanokkantapong, V., Marhaba, T.F., Pavasant, P. and Panyapinyophol, B. (2006) Characterization of haloacetic acid precursors in source water. *Journal of Environmental Management,* **80**: 214-221.

Kanokkantapong, V., Panyapinyophol, B., Wattanachira, S., Marhaba, T.F. and Pavasant, P. (2005) Characterization of natural organic matter fractionation for Bangkok water source. *Thai Environmental Journal*, **19**: 17-27.

King, W.D., Dodds, L. and Allen, A.C. (2000) Relation between stillbirth and specific chlorination byproducts in public water supplies. *Environmental Health Perspectives*, **108:** 883-886.

King, W.D, and Marrett, L.D. (1996) Case-control study of bladder cancer and chlorination byproducts in treated water (Ontario, Canada). *Cancer Causes Control,* **7**: 596-604.

Korshin, G.V., Benjamin, M.M. and Sletten, R.S. (1997) Adsorption of natural organic matter (NOM) on iron oxide: effects on NOM composition and formation of organo-halide compounds during chlorination. *Water Research*, **31**: 1643-1650.

Labanowski, J., and Feuillade, G. (2009) Combination of biodegradable organic matter quantification and XAD-fractionation as effective working parameter for the study of biodegradability in environmental and anthropic samples. *Chemosphere,* **74**: 605-611.

Leenheer, J.A. (1981) Comprehensive approach to preparative isolation and fractionation of dissolved organic carbon from natural waters and wastewaters. *Environmental Science and Technology,* **15**: 578-587.

Leenheer, J.A., and Croue, J.P. (2003) Characterizing dissolved aquatic organic matter. *Environmental Science and Technology,* **37**: 18A-26A.

Li C.W., Banjamin, M.M. and Korshin, G.V. (2000) Use of UV spectroscopy to characterize the reaction between NOM and free chlorine. *Environmental Science and Technology,* **34**: 2570-2575.

Liang, L. and Singer, P.C. (2003) Factors influencing the formation and relative distribution of haloacetic acids and trihalomethanes in drinking water. *Environmental Science and Technology*, **37**: 2920-2928.

Malcolm, R.L. (1985). Geochemistry of stream fulvic and humic substances. *Humic substances in soil, sediment and water. Geochemistry isolation and characterization*, New York, USA.

Marhaba, T.F. and Van, D. (1999) Chlorinated disinfection by-product formation potential of dissolved organic matter fractions at an ozonation water treatment plant. *Advances in Environmental Research,* **3**: 255-268.

Marhaba, T.F. and Van, D. (2000) The variation of mass and disinfection by-product formation potential of dissolved organic matter fractions along a conventional surface water treatment plant. *Journal of Hazardous Materials,* **A74**: 133-147.

Marhaba, T.F., Pu, Y., and Bengraine, K. (2003) Modified dissolved organic matter fractionation technique for natural water. *Journal of Hazardous Materials,* **B101**: 43-53.

Minear, R.A. and Amy, G.L. (1996). Disinfection by-products in water treatment. The *chemistry of their formation and control,* Florida, US.

Nieuwenhuijsen, M., Toledano, M.B., Bennett, J., Best, N., Hambly, P., de Hoogh, C., Wellesley, D., Boyd, P.A., Abramsky, L., Dattani, N., Fawell, J., Briggs, D., Jarup, L., and Elliott, P. (2008) Chlorination disinfection by-products and risk of congenital anomalies in England and Wales. *Environmental Health Perspectives,* **116**: 216-222.

Nikulaou, A.D., Kostopoulou, M.N., and Lekkas, T.D. (1999) Organic by-products of drinking water chlorination. *Global Nest: The international Journal*, **1**: 143-156.

Nova Scotia Department of Environment. (1994) Water and Wastewater Facilities and Public Drinking Water Supplies Regulation. *Environment Act*, S.N.S. 1994-95, c. 1.

Ratnaweera, H., Hiller, N., and Bunse, U. (1999) Comparison of the coagulation behavior of different Norwegian aquatic NOM sources. *Environment International*, **25**:347-355.

Rice, J.A. and MacCarthy, P. (1991) Composition of humin in stream sediments and peats. *Organic Substances and Sediments in Water, Part 1: Humic and Other Substances,* Michigan, USA.

Rook, J.J. (1974) Formation of haloform during chlorination of natural waters. *Water Treatment Exam,* **23**: 234-243.

Scott, M.J., Jones, M.N., Woof, C., Simon, B., and Tipping, E. (2001) The molecular properties of humic substances isolated from a UK upland peat system: a temporal investigation. *Environment International*, **27**: 449-462.

Sharp, E.L., Jarvis, P., Parsons, S.A. and Jefferson, B. (2006) Impact of fractional character on the coagulation of NOM. *Colloids and Surfaces A: Physiochemical Engineering Aspects,* **286**: 104-111.

Sharp, E.L., Jarvis, P., Parsons, S.A. and Jefferson, B. (2006) The impact of zeta potential on the physical properties of ferric-NOM flocs. *Environmental Science and Technology,* **40**: 3934-3940.

Sharp, E.L., Parsons, S.A., and Jefferson, B. (2005) Seasonal variations in natural organic matter and its impact on coagulation in water treatment. *Science of the Total Environment,* **363**: 183-194.

Sincero, A.P. and Sincero, G.A. (2003) Physical-Chemical treatment of water and wastewater. *CRC Press, IWA Publishing*, London, UK.

Singer, P.C. (2008) Measures of water quality impacting disinfection. *Institute of Medicine*, Washington, USA.

Swietlik, J. and Sikorska, E. (2005) Characterization of natural organic matter fractions by high pressure size-exclusion chromatography, specific UV absorbance and total luminescence spectroscopy. Polish Journal of Environmental Studies, **15**: 145-153.

USEPA (US Environmental Protection Agency), (2006) Stage 2 Disinfectants and Disinfection Byproducts Rule. *Federal Registry,* 40 CFR, Parts 9, 141, and 142.

Vadasarukkai, Y.S. (2010) Assessment of Hydraulic Performance of Flocculation Processes using Computational Fluid Dynamics (CFD). *Master of Applied Science (M.A.Sc) Thesis*, Dalhousie University, Canada.

White, M.C., Thompson, J.D., Harrington, G.W., and Singer, P.C. (1997) Evaluating criteria for enhanced coagulation compliance. *Journal of the American Water Works Association,* **89**: 64-77.

Zouboulis, A.I., Jun, W. and Katsoyiannis, I.A. (2003) Removal of humic acids by flotation. *Colloids Surfaces A: Physiochemical Engineering Aspects,* **231**: 181-193.

APPENDIX A – Raw DOC Data

Table A.1 – Dissolved organic carbon of raw water samples from the JDKWSP.

	Jun 09	Aug 09	Oct 09	Dec 09	Jan 10	Jul 10	Aug 10
RAW	2.55	2.5	2.89	2.76	2.86	2.51	2.05
HON	0.543	0.92	1.18	0.21	0.64	0.05	0.02
HOB	0.467	0.01	0.05	0.82	0.06	0.03	0.11
HOA	0.22	0.09	N/D	0.53	0.46	0.22	0.63
HIB	0.51	0.16	1.32	0.23	0.32	0.04	0.02
HIA		0.17	0.71	0.07	0.1	0.11	0.27
HIN	0.915	1.15	0.46	0.91	1.28	1.12	1.2

Table A.2 – Dissolved organic carbon of treated water samples from the JDKWSP.

	Jul 10	Aug 10
TREATED	1.9	1.48
HON	0.02	0.14
HOA	0.06	0.04
HOB	0.52	0.48
HIB	0.19	0.02
HIA	0.08	0.32
HIN	0.68	0.63

Table A.3 – Dissolved organic carbon of raw water samples from the MVWA.

	May 10	Jun 10	Aug 10	Oct 10
RAW	3.60	3.62	5.58	7.59
HON	0.20	0.02	0.20	0.26
HOB	0.07	0.05	0.20	0.16
HOA	0.92	0.74	1.86	4.82
HIB	0.04	0.22	0.04	0.55
HIA	1.50	0.05	0.60	0.10
HIN	0.99	1.92	1.78	1.70

Table A.4 – Dissolved organic carbon of filtered samples.

	May 10	Jun 10	Aug 10	Oct 10
TREATED	4.13	1.84	2.63	2.38
HON	0.11	0.15	0.18	0.21
HOB	0.04	0.12	0.32	0.21
HOA	0.17	1.28	0.63	0.90
HIB	1.36	0.09	0.05	0.51
HIA	0.07	0.31	0.77	0.05
HIN	1.62	2.94	1.69	0.51

APPENDIX B – Raw SEC data

Table B.1 – Integrated area under the elution curves of raw and filtered water samples from the JDKWSP.

	July	August
Raw	89449	73018
Treated	44612	34404
Removal	50.1%	52.9%

Table B.2 – Molecular weights of peaks identified in the samples analyzed from the JDKWSP in August 2009.

	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	Peak 6	Peak 7	Peak 8
Raw	55920	1032		557	342	252	141	
HON			617			256		98
HOB		848				243		
HOA		1015		559		226		
HIB		1006		443		221	110	
HIA		878	631			252		
HIN		909		534	374	231	120	

Table B.3 – Molecular weights of peaks identified in the samples analyzed from the JDKWSP in December 2009.

	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	Peak 6	Peak 7	Peak 8
Raw	51351	1178	713	462	257	191	128	96
HON	54863		845	494	276	175	100	
HOB			831	506		193	132	99
HOA			790	485	236		133	92
HIB		1114	733	485	299	202	126	92
HIA		941	657	453		229		94
HIN			696	500	322	191	133	96

Table B.4 – Molecular weights of peaks identified in the samples analyzed from the JDKWSP in February 2010.

	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	Peak 6	Peak 7	Peak 8
Raw	42943	1316	736	478	264	181	122	80
HON	60661	1724		524	238	178	120	82
HOB		1055	730	549	365	178	122	85
HOA		1087	736	545	438	290	128	
HIB			715	450	289		149	92
HIA		1137	637	471			124	88
HIN		1123		549	307	180	123	85

Table B.5 – Molecular weights of peaks identified in the samples analyzed from the JDKWSP in July 2010.

	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	Peak 6	Peak 7	Peak 8
Raw		1248	787	533	316	221	150	104
HON			793	540		232	155	109
HOB			707	465		236	157	112
HOA		1070	766	506	285	213	156	109
HIB		1023					155	113
HIA			826	552	330	223	154	101
HIN				501		230	154	112
Treated			842	526	317	224	155	106
HON			725	446	292	226	156	110
HOB			748	504		234	158	115
HOA			855	512	284		151	107
HIB			772	481		195		113
HIA			821	546	327	223	155	110
HIN			801	532		229	157	112

Table B.6 – Molecular weights of peaks identified in the samples analyzed from the JDKWSP in July 2010.

	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	Peak 6	Peak 7	Peak 8
Raw		1115	727	472	293	228	173	131
HON			717		370	235	167	124
HOB			696			241	172	122
HOA		884	711	505	346	238	167	136
HIB			707	570		241	171	121
HIA			764	503	322	218	167	123
HIN			591	427		236	170	127
Treated			739	488	303	228	173	129
HON			836	509	308	219	143	
HOB			683	489		244	170	125
HOA		1161	752	496	306	218	155	103
HIB			663	481	242	173	129	
HIA			781	517	328	215	165	125
HIN			655		303	242	171	124

Table B.7 – Integrated area under the elution curves of raw and filtered water samples from the MVWA.

	May	June	August	October
Raw	189037	182533	297228	485138
Filtered	50355	56639	79838	74234
Removal	73.3%	68.9%	73.1%	84.7%

Table B.8 – Molecular weights of peaks identified in the samples analyzed from the MVWA in May 2010.

	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	Peak 6	Peak 7	Peak 8	Peak 9
RAW	59342	1847	1038	787	547	340	293	165	116
HON				816	551		237	167	109
HOB				667	513		246	166	120
HOA		1452	1024	795	542	326	220	169	
HIB				760	536		237	165	118
HIA			1177	766	505	320		189	120
HIN				816	601	366	233	165	119
TREATED			1171	843	556	340	239	165	119
HON	60778			747	564	293	236	163	118
HOB				751			231	160	115
HOA			1014	810	507	292	230	162	
HIB			906	744	403	320	248	190	112
HIA				838	580	293	230	162	117
HIN					585	282	231	165	118

Table B.9 – Molecular weights of peaks identified in the samples analyzed from the MVWA in June 2010.

	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	Peak 6	Peak 7	Peak 8	Peak 9	Peak 10
RAW	58299	1707	1068	787	540	323	226	156	114	
HON				878	732		230	158	110	
HOB			1109	719	525		232	158	111	
HOA	59332	1513	1063	784	517	296	214	152	91	35
HIB			1066	699	469	300		188	109	45
HIA				818	616	352	224	159	114	
HIN				817	613	349	255	159	113	
TREATED			1009	803	544	327	227	158	113	
HON			962	742	555	305	234	162	109	62
HOB				657	510		234	158	114	
HOA			1120	807	527	286	232	159	115	
HIB			1060	789	517	316	217	139	114	54
HIA				760	565	333	230	158	112	
HIN					591	305	231	159	116	

Table B.10 – Molecular weights of peaks identified in the samples analyzed from the MVWA in August 2010.

	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	Peak 6	Peak 7	Peak 8	Peak 9
RAW	61425	1388	1146	862	588	333	215	149	98
HON				830	487	316	240	171	129
HOB				780	616	480	248	175	124
HOA	54757	1333		830	646	451	279	153	
HIB				880	700	460	303	209	108
HIA				780	502	319	217	160	118
HIN						361	216	150	104
TREATED		1386	1143	906	596	330	214	149	104
HON				730	479		279	171	138
HOB				712	495		240	170	125
HOA			1057	724	457	284	212	154	102
HIB			1021	856	678	454	202	119	
HIA				766	502	319	223	174	120
HIN						291	220	149	104

Table B.11 – Molecular weights of peaks identified in the samples analyzed from the MVWA in October 2010.

	Peak 1	Peak 2	Peak 3	Peak 4	Peak 5	Peak 6	Peak 7	Peak 8	Peak 9	Peak 10
RAW	60644	1916	1017	802	571	351	266	201	143	
HON			1439	924	606	382	282	197	146	98
HOB					569		287	208	147	
HOA	55962	1963	1066	826	577	355	249	187	119	
HIB			1331	879	599	404	280		142	
HIA			931		642	409	254	200	154	
HIN					630	407	288	205	153	
TREATED			1287	881	599	383	277	200	136	
HON				974	604	385	282	194	131	83
HOB				897	610	424	289	209	150	
HOA	68643		1435	887	600	367	257	184	130	
HIB			1186	880	592	387	276		149	
HIA				933	650	427	261	197	152	
HIN					631	402	284	205	151	

APPENDIX C – Raw DBP Data

Table C.1.1 – HAAfp compounds with associated abbreviations.

Chloroacetic Acid	CAA
Bromoacetic Acid	BAA
Dichloroacetic Acid	DCA
Trichloroacetic Acid	TCA
Bromochloroacetic Acid	BCA
Dibromoacetic Acid	DBA
Bromodichloroacetic Acid	BDCA
Chlorodibromoacetic Acid	CDBA
Tribromoacetic Acid	TBA

Table C.1 – THMfp of raw water organic fractions under plant dosing conditions at the JDKWSP, sampled in August 2009. Results are presented on a normalized yield basis (μg THM / mg DOC).

	$CHCl_3$	$CHCl_2Br$	$CHBr_2Cl$	$CHBr_3$	Total THMfp
RAW	8.48	1.20	0.45	0.00	10.12
HON	7.93	3.58	1.58	0.00	13.09
HOB	5.48	2.43	0.00	0.00	7.90
HOA	4.99	2.16	0.91	0.00	8.06
HIB	13.46	4.29	1.86	0.00	19.61
HIA	20.23	9.00	3.68	0.00	32.90
HIN	4.65	2.17	0.00	0.00	6.83

Table C.2 – HAAfp of raw water organic fractions under plant dosing conditions at the JDKWSP, sampled in August 2009. Results are presented on a normalized yield basis (μg HAA / mg DOC).

	CAA	BAA	DCA	TCA	BCA	DBA	BDCA	CDBA	TBA	Total HAAfp
RAW	2.01	0.00	4.84	0.00	1.21	0.25	0.13	0.54	0.72	9.70
HON	0.00	0.00	0.00	0.00	1.12	0.35	0.32	1.47	2.02	5.27
HOB	0.00	0.00	0.00	0.00	0.76	0.28	0.26	1.25	0.00	2.55
HOA	0.00	0.00	0.00	0.00	0.74	0.29	0.25	1.11	0.00	2.40
HIB	0.00	0.00	0.00	0.00	1.53	0.54	0.51	0.00	0.00	2.58
HIA	15.45	0.00	0.00	0.00	3.35	0.90	0.97	4.19	0.00	24.87
HIN	0.00	0.00	0.00	0.00	0.65	0.00	0.00	1.11	0.00	1.77

Table C.3 – THMfp of raw water organic fractions under plant dosing conditions at the JDKWSP, sampled in December 2009. Results are presented on a normalized yield basis (μg THM / mg DOC).

	$CHCl_3$	$CHCl_2Br$	$CHBr_2Cl$	$CHBr_3$	Total THMfp
RAW	13.00	1.68	1.36	0.00	16.04
HON	17.25	2.66	0.00	0.00	19.91
HOB	11.37	2.19	1.84	0.00	15.40
HOA	9.15	0.88	0.00	0.00	10.02
HIB	8.76	3.81	2.93	0.00	15.51
HIA	10.58	6.00	7.06	0.00	23.64
HIN	6.48	2.53	0.00	0.00	9.01

Table C.4 – HAAfp of raw water organic fractions under plant dosing conditions at the JDKWSP, sampled in December 2009. Results are presented on a normalized yield basis (μg HAA / mg DOC).

	CAA	BAA	DCA	TCA	BCA	DBA	BDCA	CDBA	TBA	Total HAAfp
RAW	2.16	0.00	6.59	0.00	2.58	0.08	0.06	0.07	0.00	11.54
HON	0.00	0.00	2.69	0.00	1.69	0.00	0.00	0.12	0.00	4.50
HOB	0.00	0.00	3.14	0.00	1.79	0.11	0.01	0.04	0.00	5.09
HOA	0.00	0.00	1.47	0.00	0.83	0.06	0.00	0.01	0.00	2.36
HIB	3.96	0.00	1.66	0.00	1.16	0.16	0.00	0.06	0.00	6.99
HIA	12.26	0.00	0.91	0.00	2.83	0.42	0.00	0.13	0.00	16.55
HIN	0.00	0.00	0.02	0.00	1.09	0.00	0.00	0.03	0.00	1.13

Table C.5 – THMfp of raw water organic fractions under plant dosing conditions at the JDKWSP, sampled in February 2010. Results are presented on a normalized yield basis (μg THM / mg DOC).

	$CHCl_3$	$CHCl_2Br$	$CHBr_2Cl$	$CHBr_3$	Total THMfp
RAW	14.42	2.03	0.00	0.00	16.45
HON	20.94	1.81	0.00	0.00	22.75
HOB	2.84	0.51	0.00	0.00	3.35
HOA	3.08	0.31	0.00	1.08	4.47
HIB	4.68	2.28	1.09	0.00	8.04
HIA	5.08	1.04	0.00	0.00	6.12
HIN	1.87	0.00	0.00	0.00	1.87

Table C.6 – HAAfp of raw water organic fractions under plant dosing conditions at the JDKWSP, sampled in February 2010. Results are presented on a normalized yield basis (μg HAA / mg DOC).

	CAA	BAA	DCA	TCA	BCA	DBA	BDCA	CDBA	TBA	Total HAAfp
RAW	3.38	0.00	12.95	0.00	3.92	0.11	0.00	0.11	0.00	20.48
HON	0.00	0.00	3.59	0.00	2.75	0.23	0.00	0.11	0.00	6.69
HOB	2.76	0.00	0.10	0.00	0.50	0.09	0.00	0.00	0.00	3.45
HOA	1.67	0.00	0.70	0.00	0.31	0.05	0.00	0.00	0.00	2.73
HIB	2.07	0.00	0.37	0.00	0.48	0.08	0.00	0.00	0.00	3.00
HIA	6.47	0.00	0.00	0.00	1.14	0.22	0.00	0.00	0.00	7.84
HIN	0.00	0.00	0.11	0.00	0.44	0.00	0.00	0.00	0.00	0.55

Table C.7 – THMfp of raw and treated water organic fractions under plant dosing conditions at the JDKWSP, sampled in July 2010. Results are presented on a normalized yield basis (µg THM / mg DOC).

	$CHCl_3$	$CHCl_2Br$	$CHBr_2Cl$	$CHBr_3$	Total THMfp
RAW	9.59	3.78	3.61	0.00	16.97
HON	11.27	9.15	9.42	0.00	29.83
HOB	12.17	15.20	15.65	0.00	43.03
HOA	6.58	2.33	2.15	0.00	11.06
HIB	0.00	0.00	12.75	0.00	12.75
HIA	9.74	5.20	4.57	0.00	19.51
HIN	0.00	7.70	13.24	0.00	20.94
TREATED	27.36	6.11	5.04	0.00	38.51
HON	8.26	9.32	8.74	0.00	26.31
HOB	1.70	8.32	8.38	0.00	18.40
HOA	0.27	0.84	0.89	0.00	2.01
HIB	0.00	0.00	5.96	0.00	5.96
HIA	0.73	2.27	2.38	0.00	5.37
HIN	0.00	14.14	47.77	0.00	61.91

Table C.8 – HAAfp of raw and filtered water organic fractions under plant dosing conditions at the JDKWSP, sampled in July 2010. Results are presented on a normalized yield basis (µg HAA / mg DOC).

	CAA	BAA	DCA	TCA	BCA	DBA	BDCA	CDBA	TBA	Total HAAfp
RAW	0.00	0.13	7.14	1.85	0.17	0.00	0.47	0.00	0.00	9.76
HON	0.00	0.62	4.01	0.94	0.00	0.00	2.01	0.00	0.00	7.57
HOB	0.00	0.00	5.58	1.42	0.00	0.00	0.00	0.00	0.00	7.00
HOA	0.00	0.00	4.98	1.25	0.33	0.00	0.00	0.00	0.00	6.56
HIB	0.00	0.63	1.02	0.13	0.00	0.00	0.00	0.00	0.00	1.78
HIA	0.00	0.00	4.42	1.24	0.22	0.00	0.61	0.00	0.00	6.49
HIN	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TREATED	0.00	0.00	5.94	1.72	0.24	0.00	0.68	0.00	0.00	8.57
HON	0.00	0.00	7.33	1.16	0.43	0.00	1.09	0.00	0.00	10.02
HOB	0.00	0.00	1.24	0.44	0.12	0.00	0.89	0.00	0.00	2.70
HOA	0.00	0.00	5.60	9.94	0.52	0.00	0.39	0.00	0.00	16.45
HIB	2.77	0.24	1.58	0.10	0.00	0.00	0.69	0.00	0.00	5.37
HIA	0.00	0.00	14.85	7.03	0.08	0.00	0.31	0.00	0.00	22.27
HIN	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table C.9 – THMfp of raw and treated water organic fractions under plant dosing conditions at the JDKWSP, sampled in August 2010. Results are presented on a normalized yield basis (μg THM / mg DOC).

	$CHCl_3$	$CHCl_2Br$	$CHBr_2Cl$	$CHBr_3$	Total THMfp
RAW	15.87	4.77	0.00	0.00	20.64
HON	3.64	0.00	36.24	0.00	39.88
HOB	6.03	4.67	0.00	0.00	10.70
HOA	2.64	0.86	0.00	0.00	3.49
HIB	12.07	12.01	11.13	0.00	35.22
HIA	4.59	2.12	1.93	0.00	8.64
HIN	0.00	0.00	0.00	0.00	0.00
TREATED	46.74	8.45	6.41	0.00	61.59
HON	0.00	0.00	0.00	0.00	0.00
HOB	8.61	12.64	12.24	0.00	33.49
HOA	3.14	1.07	1.08	0.00	5.29
HIB	4.97	14.29	16.54	0.00	35.80
HIA	3.87	1.89	1.74	0.00	7.50
HIN	0.71	0.00	0.00	0.00	0.71

Table C.10 – HAAfp of raw and filtered water organic fractions under plant dosing conditions at the JDKWSP, sampled in August 2010. Results are presented on a normalized yield basis (μg HAA / mg DOC).

	CAA	BAA	DCA	TCA	BCA	DBA	BDCA	CDBA	TBA	Total HAAfp
RAW	0.00	0.00	7.00	2.52	0.32	0.00	0.68	0.00	0.00	10.52
HON	8.84	0.88	1.04	1.52	1.04	0.00	0.00	0.00	0.00	13.32
HOB	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
HOA	0.00	0.00	1.39	0.41	0.00	0.00	0.00	0.00	0.00	1.80
HIB	0.56	0.00	3.35	3.95	0.35	0.00	1.85	0.00	0.00	10.07
HIA	0.00	0.00	2.99	0.91	0.14	0.00	0.26	0.00	0.00	4.30
HIN	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
TREATED	0.00	0.00	7.95	11.72	0.45	0.00	1.54	0.00	3.78	25.45
HON	0.45	0.04	8.93	0.20	0.16	0.00	0.00	0.71	1.28	11.76
HOB	0.00	0.00	2.24	1.19	0.13	0.00	0.00	0.00	0.00	3.56
HOA	0.86	0.00	6.31	11.98	0.53	0.00	0.87	0.00	0.00	20.56
HIB	3.66	0.00	1.28	0.98	0.11	0.00	0.00	0.00	0.00	6.03
HIA	0.60	0.00	14.41	14.66	0.61	0.00	0.56	0.00	0.00	30.84
HIN	0.00	0.00	1.65	0.24	0.00	0.00	1.79	0.00	0.00	3.68

Table C.11 – THMfp of raw and treated water organic fractions under uniform conditions from the JDKWSP, sampled in August 2010. Results are presented on a normalized yield basis (µg THM / mg DOC).

	$CHCl_3$	$CHCl_2Br$	$CHBr_2Cl$	$CHBr_3$	Total THMfp
RAW	67.32	7.08	4.24	0.00	78.64
HON	9.80	0.00	0.00	0.00	9.80
HOB	14.91	5.22	4.55	0.00	24.68
HOA	153.78	3.93	0.89	0.00	158.61
HIB	23.89	12.37	11.63	0.00	47.89
HIA	27.78	6.51	3.04	0.00	37.33
HIN	15.98	8.55	7.59	0.00	32.12
TREATED	63.86	9.07	6.45	0.00	79.39
HON	22.92	4.91	2.19	0.00	30.01
HOB	15.80	12.93	12.33	0.00	41.07
HOA	47.44	3.50	1.18	0.13	52.26
HIB	15.78	14.78	14.12	0.00	44.69
HIA	19.77	5.21	2.70	0.00	27.68
HIN	3.09	0.00	0.72	0.00	3.81

Table C.12 – HAAfp of raw and treated water organic fractions under uniform conditions from the JDKWSP, sampled in August 2010. Results are presented on a normalized yield basis (µg HAA / mg DOC).

	CAA	BAA	DCA	TCA	BCA	DBA	BDCA	CDBA	TBA	Total HAAfp
RAW	0.56	0.00	20.05	32.23	0.78	0.00	1.64	0.00	0.00	55.26
HON	8.20	1.44	4.48	6.96	1.28	0.00	6.44	18.76	0.00	47.56
HOB	0.00	0.00	1.62	0.41	0.00	0.00	0.00	0.00	0.00	2.03
HOA	2.06	0.03	34.23	13.31	0.83	0.00	3.63	0.28	0.54	54.89
HIB	1.78	0.00	8.68	10.74	0.37	0.00	2.99	3.55	0.00	28.11
HIA	1.19	0.04	8.14	17.74	1.53	0.00	4.25	0.92	0.00	33.81
HIN	0.34	0.00	2.53	2.18	0.00	0.00	1.03	0.00	0.00	6.09
TREATED	0.55	0.00	16.16	19.79	0.78	0.00	1.97	0.00	0.00	39.26
HON	0.42	0.28	14.97	3.69	1.11	0.09	0.92	0.79	1.27	23.54
HOB	0.00	0.00	4.37	4.23	0.01	0.00	1.76	0.00	0.00	10.37
HOA	1.23	0.02	19.96	15.34	1.17	0.00	4.16	0.36	0.70	42.95
HIB	0.00	0.00	4.22	5.26	0.12	0.00	0.00	0.00	0.00	9.60
HIA	1.29	0.05	22.95	20.26	1.79	0.06	3.96	0.76	0.00	51.13
HIN	0.00	0.44	9.32	7.71	0.56	0.00	0.21	0.00	0.00	18.24

Table C.13 – THMfp of raw and treated water organic fractions under plant dosing conditions at the MVWA, sampled in May 2010. Results are presented on a normalized yield basis (μg THM / mg DOC).

	$CHCl_3$	$CHCl_2Br$	$CHBr_2Cl$	$CHBr_3$	Total THMfp
RAW	24.05	1.62	1.06	0.00	26.73
RHON	11.98	1.53	0.93	0.00	14.44
RHOB	15.79	9.68	4.91	0.00	30.38
RHOA	1.49	0.31	0.21	0.00	2.01
RHIB	0.00	0.00	5.28	0.00	5.29
RHIA	0.54	0.29	0.14	0.00	0.97
RHIN	0.00	0.00	3.68	0.00	3.67
FILTERED	10.41	1.47	0.87	0.00	12.76
FHON	11.70	2.81	1.77	0.00	16.28
FHOB	2.97	8.55	5.37	0.00	16.89
FHOA	19.38	1.77	1.19	0.00	22.35
FHIB	0.00	0.00	0.15	0.00	0.15
FHIA	2.15	9.74	9.97	0.00	21.86
FHIN	0.00	0.00	2.27	0.00	2.27

Table C.14 – HAAfp of raw and filtered water organic fractions under plant dosing conditions at the MVWA, sampled in May 2010. Results are presented on a normalized yield basis (µg HAA / mg DOC).

	CAA	BAA	DCA	TCA	BCA	DBA	BDCA	CDBA	TBA	Total HAAfp
RAW	0.24	0.00	12.30	13.49	0.00	0.00	0.31	1.23	3.27	30.83
RHON	0.00	0.00	5.20	2.58	0.00	0.00	0.28	1.14	3.04	12.24
RHOB	0.00	0.00	7.67	6.77	1.69	0.00	2.22	3.60	0.00	21.95
RHOA	0.00	0.00	0.33	0.10	0.00	0.00	0.02	0.14	0.29	0.89
RHIB	0.00	0.00	0.08	0.21	0.00	0.00	0.00	6.23	0.00	6.52
RHIA	0.03	0.00	0.54	0.15	0.01	0.00	0.03	0.09	0.19	1.03
RHIN	0.00	0.00	0.48	0.02	0.00	0.00	0.00	4.49	0.00	4.99
FILTERED	0.00	0.00	5.02	2.88	0.00	0.00	0.13	0.60	1.23	9.87
FHON	0.00	0.00	5.97	3.67	0.00	0.00	0.51	2.12	5.65	17.92
FHOB	0.00	0.98	2.47	1.87	0.28	0.00	1.60	5.61	14.73	27.53
FHOA	0.00	0.00	6.30	9.21	0.00	0.00	0.33	1.39	3.71	20.94
FHIB	0.00	0.00	0.05	0.00	0.00	0.00	0.01	0.10	0.21	0.37
FHIA	0.00	0.00	2.26	1.82	1.86	0.34	2.52	4.17	9.48	22.44
FHIN	0.00	0.00	0.00	0.00	0.00	0.00	0.00	1.54	3.13	4.67

Table C.15 – THMfp of raw and treated water organic fractions under uniform conditions at the MVWA, sampled in May 2010. Results are presented on a normalized yield basis (μg THM / mg DOC).

	$CHCl_3$	$CHCl_2Br$	$CHBr_2Cl$	$CHBr_3$	Total THMfp
RAW	55.65	1.80	1.08	0.00	58.53
RHON	16.19	1.59	0.94	0.00	18.72
RHOB	18.31	10.10	4.71	0.00	33.12
RHOA	65.26	0.53	0.21	0.00	65.99
RHIB	0.56	7.17	5.15	0.00	12.88
RHIA	6.33	5.62	2.42	0.00	14.37
RHIN	0.00	5.23	3.76	0.00	8.99
FILTERED	13.61	1.47	0.92	0.00	15.99
FHON	3.32	2.51	1.74	0.00	7.58
FHOB	6.05	9.22	5.32	0.00	20.59
FHOA	38.64	1.90	1.19	0.00	41.72
FHIB	0.01	0.21	0.14	0.00	0.36
FHIA	5.41	10.68	6.45	0.00	22.54
FHIN	0.00	3.16	2.26	0.00	5.42

Table C.16 – HAAfp of raw and filtered water organic fractions under uniform conditions at the MVWA, sampled in May 2010. Results are presented on a normalized yield basis (µg HAA / mg DOC).

	CAA	BAA	DCA	TCA	BCA	DBA	BDCA	CDBA	TBA	Total HAAfp
RAW	0.98	0.00	29.05	36.87	0.00	0.00	0.40	1.23	3.27	71.81
RHON	0.00	0.00	7.12	4.59	0.00	0.00	0.30	1.14	3.04	16.19
RHOB	0.00	0.00	8.55	9.46	1.59	0.00	2.52	3.62	0.00	25.74
RHOA	1.11	0.00	23.26	9.21	0.00	0.00	0.12	0.14	0.30	34.15
RHIB	0.00	0.00	1.70	1.01	0.00	0.00	0.00	6.20	16.52	25.43
RHIA	0.18	0.07	1.98	3.36	1.23	0.25	1.63	0.32	0.22	9.23
RHIN	0.00	0.00	1.17	0.34	0.00	0.00	0.00	4.46	0.00	5.97
FILTERED	0.11	0.00	4.95	2.99	0.00	0.00	0.26	1.07	2.85	12.23
FHON	0.00	0.00	3.28	2.39	0.00	0.00	0.20	1.19	0.00	7.06
FHOB	0.00	0.09	3.77	2.92	0.24	0.00	1.61	5.63	0.00	14.26
FHOA	1.51	0.00	13.91	34.12	0.00	0.00	0.44	1.39	3.75	55.11
FHIB	0.00	0.00	0.17	0.02	0.00	0.00	0.04	0.18	0.47	0.87
FHIA	0.00	0.00	3.44	3.79	1.60	0.00	2.86	4.08	9.35	25.12
FHIN	0.00	0.00	0.85	0.25	0.00	0.00	0.00	2.74	7.29	11.13

Table C.17 – THMfp of raw and treated water organic fractions under plant dosing conditions at the MVWA, sampled in June 2010. Results are presented on a normalized yield basis (µg THM / mg DOC).

	$CHCl_3$	$CHCl_2Br$	$CHBr_2Cl$	$CHBr_3$	Total THMfp
RAW	24.08	1.62	0.00	0.00	25.70
RHON	0.11	11.10	9.66	0.00	20.87
RHOB	49.67	15.18	7.35	0.00	72.19
RHOA	3.15	0.37	0.31	0.00	3.84
RHIB	0.00	0.00	1.07	0.00	1.07
RHIA	8.77	16.04	15.11	1.68	41.60
RHIN	0.00	0.00	2.37	0.00	2.37
FILTERED	40.29	3.52	2.53	0.00	46.34
FHON	12.02	2.70	1.69	0.00	16.42
FHOB	8.38	3.04	2.11	0.00	13.52
FHOA	0.97	0.37	0.22	0.00	1.56
FHIB	0.00	2.86	2.51	0.00	5.37
FHIA	6.90	2.03	0.89	0.00	9.83
FHIN	0.32	0.00	1.55	0.00	1.87

Table C.18 – HAAfp of raw and filtered water organic fractions under plant dosing conditions at the MVWA, sampled in June 2010. Results are presented on a normalized yield basis (µg HAA / mg DOC).

	CAA	BAA	DCA	TCA	BCA	DBA	BDCA	CDBA	TBA	Total HAAfp
RAW	2.05	0.43	10.49	4.59	0.57	0.21	0.60	1.73	3.34	24.00
RHON	0.00	0.00	7.31	3.14	3.35	1.44	3.92	12.61	24.66	56.43
RHOB	0.00	1.59	3.25	1.54	1.82	0.74	2.05	6.55	12.88	30.41
RHOA	0.59	0.00	2.19	0.71	0.12	0.05	0.13	0.41	0.80	5.00
RHIB	0.00	0.32	0.77	0.20	0.37	0.00	0.00	1.39	2.70	5.76
RHIA	0.00	4.85	6.87	3.29	4.64	3.06	3.09	6.50	11.82	44.12
RHIN	0.00	0.00	1.28	0.37	0.78	0.34	0.90	3.05	6.00	12.73
FILTERED	0.17	0.00	19.23	7.98	0.00	0.00	0.34	1.38	2.76	31.86
FHON	0.00	0.00	2.18	0.49	0.00	0.00	0.18	0.85	1.74	5.44
FHOB	0.00	0.00	1.81	0.76	0.00	0.00	0.20	1.09	0.00	3.86
FHOA	0.00	0.00	2.82	0.86	0.39	0.03	0.08	0.11	0.20	4.48
FHIB	0.00	0.00	1.85	0.00	0.00	0.00	0.00	1.35	2.77	5.97
FHIA	0.15	0.00	0.33	0.14	0.00	0.00	0.10	0.43	0.86	2.01
FHIN	0.00	0.00	0.02	0.00	0.00	0.00	0.00	0.84	0.00	0.86

Table C.19 – THMfp of raw and treated water organic fractions under uniform conditions at the MVWA, sampled in June 2010. Results are presented on a normalized yield basis (µg THM / mg DOC).

	$CHCl_3$	$CHCl_2Br$	$CHBr_2Cl$	$CHBr_3$	Total THMfp
RAW	94.54	1.93	1.26	0.00	97.73
RHON	52.91	11.53	9.64	0.00	74.08
RHOB	72.80	17.02	7.02	0.00	96.83
RHOA	125.76	0.65	0.34	0.00	126.75
RHIB	0.00	0.00	0.00	0.00	0.00
RHIA	75.22	42.85	9.80	0.00	127.87
RHIN	0.00	2.70	2.08	0.00	4.78
FILTERED	47.03	3.58	2.48	0.00	53.09
FHON	26.97	3.12	1.68	0.00	31.77
FHOB	15.30	3.36	2.10	0.00	20.76
FHOA	32.34	1.21	0.28	0.00	33.83
FHIB	0.00	2.95	2.52	0.00	5.46
FHIA	29.00	2.39	0.82	0.00	32.21
FHIN	20.22	2.20	1.56	0.00	23.98

Table C.20 – HAAfp of raw and filtered water organic fractions under uniform conditions at the MVWA, sampled in June 2010. Results are presented on a normalized yield basis (µg HAA / mg DOC).

	CAA	BAA	DCA	TCA	BCA	DBA	BDCA	CDBA	TBA	Total HAAfp
RAW	2.02	0.40	23.94	28.99	0.59	0.22	0.64	1.65	3.24	61.69
RHON	6.38	0.00	10.49	3.86	3.28	1.40	3.69	12.52	24.56	66.17
RHOB	2.35	1.70	6.22	3.89	2.28	0.76	2.43	6.59	12.89	39.11
RHOA	0.49	0.09	5.83	2.67	0.12	0.06	0.15	0.40	0.80	10.60
RHIB	0.00	0.00	3.05	0.39	0.38	0.16	0.42	1.38	2.71	8.48
RHIA	2.25	1.31	3.08	1.57	1.78	0.71	2.12	5.94	11.59	30.37
RHIN	0.00	0.00	2.23	0.72	0.80	0.39	0.96	3.07	6.01	14.18
FILTERED	0.77	0.00	15.74	8.97	0.00	0.00	0.34	1.35	2.75	29.92
FHON	0.00	0.00	9.51	3.06	0.13	0.00	0.34	0.87	1.76	15.67
FHOB	0.00	0.00	3.13	1.29	0.00	0.14	0.24	1.10	2.22	8.12
FHOA	1.13	0.00	3.36	3.62	0.31	0.00	0.24	0.11	0.21	8.98
FHIB	0.00	0.76	3.62	0.68	0.89	0.00	0.00	0.00	0.00	5.95
FHIA	1.13	0.00	1.46	0.44	0.00	0.00	0.10	0.42	0.86	4.41
FHIN	2.25	0.00	4.37	2.45	0.66	0.27	0.72	2.00	3.94	16.65

Table C.21 – THMfp of raw and treated water organic fractions under plant dosing conditions at the MVWA, sampled in August 2010. Results are presented on a normalized yield basis (µg THM / mg DOC).

	CHCl₃	CHCl₂Br	CHBr₂Cl	CHBr₃	Total THMfp
RAW	11.15	1.84	0.00	0.00	12.99
RHON	20.15	4.49	3.79	0.00	28.43
RHOB	1.73	3.20	2.72	0.00	7.66
RHOA	0.79	0.26	0.28	0.00	1.33
RHIB	19.85	19.85	0.00	0.00	39.69
RHIA	2.74	0.89	0.87	0.00	4.50
RHIN	0.00	0.00	0.00	0.00	3.67
FILTERED	21.70	3.41	3.16	0.00	28.27
FHON	22.42	7.75	5.87	0.00	36.04
FHOB	1.55	1.95	1.81	0.00	5.31
FHOA	7.86	0.92	0.00	0.00	8.78
FHIB	17.17	5.29	6.11	0.00	28.56
FHIA	4.15	0.76	0.00	0.00	4.91
FHIN	0.00	0.00	0.00	0.00	0.00

Table C.22 – HAAfp of raw and filtered water organic fractions under plant dosing conditions at the MVWA, sampled in August 2010. Results are presented on a normalized yield basis (µg HAA / mg DOC).

	CAA	BAA	DCA	TCA	BCA	DBA	BDCA	CDBA	TBA	Total HAAfp
RAW	0.00	0.00	6.45	2.99	0.02	0.00	0.00	0.00	0.00	9.46
RHON	0.00	0.00	5.44	3.04	0.27	0.00	0.68	1.20	0.00	10.62
RHOB	0.21	0.00	0.77	0.63	0.24	0.00	0.51	0.83	0.00	3.19
RHOA	0.00	0.00	0.50	0.17	0.04	0.00	0.00	0.00	0.00	0.71
RHIB	0.00	0.00	3.47	6.25	0.00	0.00	0.00	0.00	0.00	9.72
RHIA	0.09	0.00	2.07	0.86	0.02	0.00	0.12	0.00	0.00	3.17
RHIN	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
FILTERED	0.00	0.00	7.21	5.13	0.13	0.00	0.49	0.00	0.00	12.95
FHON	0.00	0.00	5.51	3.86	0.67	0.00	1.25	1.82	0.00	13.11
FHOB	0.00	0.00	0.25	0.19	0.12	0.00	0.27	0.53	0.00	1.35
FHOA	0.05	0.00	2.97	1.11	0.28	0.00	0.13	0.29	0.51	5.34
FHIB	0.00	0.00	2.36	3.47	0.00	0.00	0.72	0.00	0.00	6.55
FHIA	0.00	0.00	1.68	0.91	0.03	0.00	0.12	0.22	0.42	3.38
FHIN	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00

Table C.23 – THMfp of raw and treated water organic fractions under uniform conditions at the MVWA, sampled in August 2010. Results are presented on a normalized yield basis (μg THM / mg DOC).

	$CHCl_3$	$CHCl_2Br$	$CHBr_2Cl$	$CHBr_3$	Total THMfp
RAW	58.01	2.16	0.00	0.00	60.18
RHON	26.14	4.72	3.96	0.00	34.82
RHOB	2.42	3.24	2.48	0.00	8.15
RHOA	85.08	1.11	0.29	0.00	86.48
RHIB	34.49	5.91	0.00	0.00	40.40
RHIA	24.49	2.19	1.01	0.00	27.69
RHIN	5.59	6.42	6.76	0.00	18.77
FILTERED	31.41	3.60	0.00	0.00	35.01
FHON	24.99	7.77	5.90	0.00	38.65
FHOB	1.69	1.92	1.83	0.00	5.43
FHOA	62.83	2.42	0.86	0.00	66.11
FHIB	41.47	5.64	0.00	0.00	47.12
FHIA	16.01	1.51	0.75	0.00	18.27
FHIN	0.60	9.03	13.23	0.00	22.85

Table C.24 – HAAfp of raw and filtered water organic fractions under uniform conditions at the MVWA, sampled in August 2010. Results are presented on a normalized yield basis (μg HAA / mg DOC).

	CAA	BAA	DCA	TCA	BCA	DBA	BDCA	CDBA	TBA	Total HAAfp
RAW	0.82	0.00	24.97	22.90	0.06	0.00	0.38	0.00	0.00	49.12
RHON	1.45	0.00	7.40	6.89	0.28	0.00	0.88	0.00	0.00	16.90
RHOB	0.00	0.00	1.04	1.15	0.23	0.00	0.57	0.81	0.00	3.80
RHOA	1.41	0.03	19.34	6.43	0.31	0.00	0.90	0.09	0.00	28.50
RHIB	0.00	0.00	5.82	11.29	0.00	0.00	0.00	0.00	0.00	17.11
RHIA	0.63	0.00	7.67	11.09	0.43	0.00	1.30	0.32	0.00	21.44
RHIN	0.00	0.00	1.20	1.23	0.00	0.00	0.00	0.00	0.00	2.42
FILTERED	0.29	0.00	8.92	10.06	0.18	0.00	0.52	0.00	0.00	19.97
FHON	1.88	0.00	7.01	6.21	0.77	0.00	1.56	1.80	0.00	19.24
FHOB	0.18	0.00	0.39	0.36	0.12	0.00	0.30	0.52	0.00	1.88
FHOA	1.17	0.00	15.04	13.25	0.67	0.00	1.27	0.27	0.00	31.67
FHIB	2.19	0.00	5.87	7.41	0.00	0.00	0.00	0.00	0.00	15.47
FHIA	0.45	0.00	3.49	7.49	0.22	0.00	0.52	0.23	0.00	12.40
FHIN	0.00	0.00	0.79	1.10	0.00	0.00	0.00	0.00	0.00	1.89

Table C.25 – THMfp of raw and treated water organic fractions under plant dosing conditions at the MVWA, sampled in October 2010. Results are presented on a normalized yield basis (μg THM / mg DOC).

	$CHCl_3$	$CHCl_2Br$	$CHBr_2Cl$	$CHBr_3$	Total THMfp
RAW	16.86	0.42	0.35	0.00	17.64
RHON	19.88	2.25	0.95	0.00	23.09
RHOB	0.00	0.00	0.69	0.00	0.69
RHOA	2.81	0.08	0.06	0.00	2.96
RHIB	4.78	4.78	0.00	0.00	9.56
RHIA	9.49	4.69	2.51	0.00	16.69
RHIN	4.51	0.30	0.14	0.00	3.67
FILTERED	33.80	1.48	2.49	0.00	37.77
FHON	19.58	1.82	0.69	0.00	22.09
FHOB	4.95	2.93	0.83	0.00	8.70
FHOA	5.38	0.21	0.25	0.00	5.85
FHIB	3.51	0.14	0.16	0.00	3.81
FHIA	10.40	11.51	9.24	0.00	31.14
FHIN	1.33	0.83	0.94	0.00	3.10

Table C.26 – HAAfp of raw and filtered water organic fractions under plant dosing conditions at the MVWA, sampled in October 2010. Results are presented on a normalized yield basis (µg HAA / mg DOC).

	CAA	BAA	DCA	TCA	BCA	DBA	BDCA	CDBA	TBA	Total HAAfp
RAW	0.52	0.03	7.22	7.62	0.07	0.04	0.00	0.00	0.00	15.51
RHON	0.00	0.10	4.73	4.11	0.43	0.05	0.55	0.00	0.00	9.96
RHOB	0.99	0.11	0.34	0.19	0.07	0.06	0.50	1.45	0.00	3.70
RHOA	0.09	0.02	1.03	0.37	0.02	0.01	0.06	0.00	0.00	1.61
RHIB	0.15	0.01	0.30	0.42	0.02	0.00	0.08	0.00	0.00	0.99
RHIA	0.98	0.51	3.70	4.66	0.83	0.15	1.68	0.00	0.00	12.50
RHIN	0.00	0.02	0.34	0.26	0.03	0.00	0.00	0.00	0.00	0.65
FILTERED	1.21	0.00	13.89	10.81	0.28	0.09	0.00	0.00	0.00	26.28
FHON	0.00	0.13	3.90	2.60	0.31	0.06	0.39	0.00	2.01	9.40
FHOB	0.43	0.16	0.92	0.57	0.20	0.04	0.00	0.00	0.00	2.33
FHOA	0.11	0.01	1.90	1.09	0.05	0.00	0.09	0.00	0.00	3.26
FHIB	0.13	0.01	0.20	0.26	0.02	0.00	0.00	0.00	0.00	0.62
FHIA	0.00	0.77	4.07	3.47	1.84	0.68	3.00	5.36	0.00	19.20
FHIN	0.23	0.04	0.26	0.22	0.05	0.02	0.00	0.00	0.00	0.82

Table C.27 – THMfp of raw and treated water organic fractions under uniform conditions at the MVWA, sampled in October 2010. Results are presented on a normalized yield basis (µg THM / mg DOC).

	CHCl₃	CHCl₂Br	CHBr₂Cl	CHBr₃	Total THMfp
RAW	88.63	0.64	0.24	0.00	89.51
RHON	31.11	2.92	0.56	0.00	34.59
RHOB	22.12	2.63	0.86	0.00	25.60
RHOA	118.99	0.62	0.06	0.00	119.67
RHIB	21.28	0.17	0.08	0.00	21.54
RHIA	16.55	5.48	3.12	0.00	25.15
RHIN	32.40	0.57	0.15	0.00	33.13
FILTERED	51.30	1.71	1.06	0.00	54.07
FHON	23.94	1.95	0.67	0.00	26.56
FHOB	19.78	4.11	0.53	0.00	24.42
FHOA	106.04	1.11	0.83	0.00	107.98
FHIB	11.51	0.15	0.20	0.00	11.86
FHIA	12.14	10.80	6.66	0.00	29.60
FHIN	13.83	1.16	0.24	0.00	15.23

Table C.28 – HAAfp of raw and filtered water organic fractions under uniform conditions at the MVWA, sampled in October 2010. Results are presented on a normalized yield basis (µg HAA / mg DOC).

	CAA	BAA	DCA	TCA	BCA	DBA	BDCA	CDBA	TBA	Total HAAfp
RAW	0.91	0.00	46.01	19.60	0.11	0.06	0.42	0.00	0.00	67.12
RHON	0.00	0.10	6.56	13.54	0.49	0.06	0.91	0.00	0.00	21.66
RHOB	1.43	0.06	2.92	3.38	0.22	0.00	0.62	0.00	0.00	8.64
RHOA	1.32	0.04	19.61	6.28	0.12	0.07	0.43	0.00	0.00	27.88
RHIB	2.07	0.02	4.39	1.35	0.02	0.00	0.00	0.00	0.00	7.83
RHIA	1.54	0.30	5.37	8.14	0.92	0.12	2.22	2.59	0.00	21.19
RHIN	1.96	0.03	1.96	0.80	0.03	0.00	0.00	0.00	0.00	4.77
FILTERED	1.57	0.12	18.33	24.67	0.24	0.08	0.71	0.00	0.00	45.71
FHON	0.00	0.12	5.80	6.47	0.38	0.05	0.00	0.00	0.00	12.82
FHOB	1.38	0.09	2.37	1.58	0.24	0.05	0.00	0.00	0.00	5.70
FHOA	0.91	0.04	20.49	7.88	0.19	0.07	0.58	0.00	0.00	30.15
FHIB	0.95	0.00	1.42	0.59	0.01	0.01	0.00	0.00	0.00	2.98
FHIA	2.64	0.65	5.31	5.90	2.08	0.44	3.94	5.50	0.00	26.45
FHIN	1.15	0.02	1.45	0.67	0.06	0.02	0.00	0.00	0.00	3.38